PULSED-ELECTROKINETIC REMEDIATION OF MIXED HEAVY METALS CONTAMINATED SOIL

BY

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Dedicated to my beloved parents

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LIST OF ABBREVIATIONS

2FI	:	2 Factor Interaction
3FD	:	3 level factorial design
ANOVA	:	Analysis of Variance
ASTM	:	American Society of Testing and Materials
BBD	:	Box-Behnken Design
B/C	:	Bentonite and Clay ratio
BET	:	Brunauer-Emmet-Teller
CCD	:	Central Composite Design
DC	:	Direct Current
DD	:	Doehlert Design
EC	:	Electrical Conductivity
EPA	:	Envpironmental Protection Agency
EKR	:	Electrokinetic Remediation
ICP- OES	:	Inductively Coupled Plasma Optical Emission Spectrometer
PDC	:	Pulse duty cycle
KFUPM	:	King Fahd University of Petroleum and Minerals
KSA	:	Kingdom of Saudi Arabia
RSM	:	Response Surface Methodology
Rp	:	Response
USA	:	United States of America
V.G	:	Voltage gradient

ABSTRACT

Full Name : [Abdullahi Kilaco Usman]

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Electrokinetic study was carried out to investigate the effect of voltage gradient, pulse duty cycle and bentonite/clay ratio on the energy consumption and removal efficiencies of mixed heavy metals (Cr, Cd, Cu, Hg and Pb) contaminated soil. Thirteen (13) experiments were conducted based on Box-Behnken Design and each experiment lasted for 3 weeks at an initial heavy metals concentration of 100mg/l each. The results were used in modeling of heavy metals removal efficiencies and energy consumption of the process with the aid of Design Expert Software. The overall sequence of factors degree of influence on the investigated responses is Voltage gradient >Bentonite/clay> Pulse duty cycle. Numerical Optimization reveals the optimum energy consumption of 308kwh/m^3 of treated soil and removal efficiency for Cd, Cr, Cu, Hg, and Pb were arrived at 27.16, 92.78, 54.71, 43.58 and 16.43 respectively at operating conditions of bentonite/clay ratio of 0.1, 0.3 and 0.5, voltage gradient of 0.2, 0.4 and 0.6 and pulse duty cycle of 0.5, 0.7 and 0.9. Increase in bentonite ratio was found to decrease removal efficiency due to its high surface area favoring adsorption while increases in voltage gradient and pulse duty cycle were found to increase the removal efficiency. Increase in both voltage gradient and pulse duty cycle was found to increase the energy consumption but bentonite ratio was found to have little or no effect on it. Voltage gradient increase was also found to increase the electrical conductivity and pH of the soil

ملخص الرسالة

الاسم الكامل: عبدالله كيلاكو عثمان

عنوان الرسالة: معالجة التربة الملوثة بخليط من المعادن الثقيلة بإستخدام تقنية التيار الحركي

التخصص: الهندسة المدنية

تاريخ الدرجة العلمية: إبريل 2015 م

في هذا البحث، تم دراسة معالجة التربة الملوثة بخليط من المعادن الثقيلة بإستخدام تقنية التيار الحركي حيث أجريت 13 تجربة بناء علي تصميم مربع بونكين لدراسة تأثير ثلاثة عوامل وهي كالتالي: تدرج الجهد الكهربائي، نبض التيار الكهربائي، و نسبة خلط البنتونايت الى الطين على استهلاك الطاقة الكهربائية ونسبة الإزالة عند معالجة التربة الملوثة بخليط من المعادن الثقيلة (الكروميوم، الكادميوم، النحاس، الزئبق، والرصاص). صممت هذه التجارب باستخدام برنامج Expert وكل تجربة تم تشغيلها لمده ثلاثة اسابيع مع تراكيز اولية ثابتة للمعادن الثقيلة 100 ملجم/ لتر من كل عنصر.

تم عمل نموذج لدراسة تأثير كفاءه إزالة المعادن الثقيلة من التربة الملوثة و نسبة استهلاك الطاقة الكهربائية بتدرج الجهد الكهربائي، نبض التيار الكهربائي، و نسبة الخلط بين كل من الطين والبنتونايت بإستخدام النتائج التي تم الحصول عليها من التجارب المعملية. حيث انه وجد ان كفاءة إزالة الملوثات و معدل استهلاك الطاقة الكهربائية تتأثربدرجة رئيسية بعامل تدرج الجهد الكهربائي متبوعا بتغير نسبة خلط البنتونايت الى الطين يليها عامل نبض التيار الكهربائي. و بإستخدام اسلوب التحسين العددي تم التوصل الى ان القيمة المثالية لاستهلاك الطاقة الكهربائية كانت 308 كيلوات ساعة /م^3 من التربة المعالجة مع نسبة إزالة لكل من الكادميوم، الكروميوم، النحاس، الزئبق والرصاص كالتالي: 27.16، 92.78، 54.71، 43.58 و 16.43 على الترتيب، عند الظروف الآتيه: نسبة خلط البنتونايت الى الطين(0.1, 0.3 ,0.5)، تدرج الجهد الكهربائي (0.2,0.4,0.6)، نبض التيار الكهربائي(0.9, 0.7 ,0.5). حيث وجد انه كلما زادت نسبة البنتونايت الى الطين نقصت كفاءة المعالجة بالطاقة الكهربائية وذلك يعزى الى المساحة السطحية الكبيرة للبنتونايت والتي تكون مفضلة في عملية المعالجة بالامتصاص، بينما الزيادة في كل من تدرج الجهد الكهربائي و نبض التيار الكهربائي تؤدي الى زيادة في كفاءة المعالجة بالطاقة الكهربائية مع زيادة في استهلاك الطاقة الكهربائية. وجد ايضا انه مع الزيادة في الجهد الكهربائي هنالك زيادة في خاصية التوصيل الكهربائي للتربة و درجة الحموضة.

CHAPTER 1

INTRODUCTION

In recent years, massive modernization and rapid industrialization has been going on in Saudi Arabia. One of the major concerns of this development to the environment is the improper releases of high amounts of different types of toxic contaminants such as “heavy metals” into the subsurface as a result of unethical industrial practices and handling of chemicals and waste materials. Currently, with groundwater resources accounting for more than 81.5 % of Saudi Arabian water supply, the vulnerability of soil, subsoil and groundwater to contamination should be treated as a potential problem not to be overlooked. This is due to the potential dangers that heavy metals pose to public health and the environment in a short and long-term circumstances [1]. Hence, exploring novel and promising cost effective technologies that are viable in the remediation of such contaminated sites becomes unavoidable for effective environmental sustenance of the kingdom.

Globally, a number of in-situ and ex-situ soil remediation technologies were developed to clean polluted soils for removing heavy metals from soil water. Even though heavy metals could be degraded by indigenous microorganisms in the soil water complex, however, the fact that biological means are ineffective removal techniques of majority of heavy metals due to bio-resistant nature. As

consequence, a number of physico-chemical remediation technologies have been proposed for treatment of soils, leachate, wastewater, and groundwater contaminated with heavy metals. Among the existing technologies, electrokinetics remediation (EKR) techniques have attracted increased interests due to number of advantages they offer over other techniques like remediation of low permeability soils [2, 3]. However, EKR are usually complex process that requires high technicality and also take long period of time thereby consuming huge amount of electricity to ensure remediation effectiveness and success. Consequently a number researchers dissipated significant efforts in attempting to understand strategies for improving and enhancing the effectiveness of EKR while reducing the treatment time (as well as the energy consumption) in order to make EKR more competitive in terms of cost-effectiveness. These strategies include addition of chelating reagents and surfactant, pH conditioning of electrolytes, using ion selective membrane, polarity reversal, pulsed voltage and integrating EKR with other remediation techniques (hybrid techniques) like lasagna [3] and so on.

In this research, pulsed electrokinetic remediation of mixed-heavy metals contaminated soil was investigated, three factors are considered; clay and bentonite ratio, voltage gradient and pulse duty cycle at varying conditions. This research is meant to investigate the effect of the factors on the removal efficiencies of the individual contaminants and energy consumption. This research will also investigate the effect of the factors of concern on soil pH, soil electrical conductivity and electroosmotic volume.

CHAPTER 2

LITERATURE REVIEW

Due to the millions of tones of generated toxic chemicals and wastes and cases of hundreds of contaminated sites worldwide annually reported, the remediation of toxic wastes contaminated sites has become an exigent and top priority to researchers, environmentalist and regulatory bodies. For instance, in the USA alone, several hundred site contaminated with toxic waste were uncovered and millions of dollars have been spent for remediating such sites [4]. Hence past decades have witnessed a number of investigations and emergence of new techniques for removal of contaminants from soils that could help in cleaning contaminated groundwater and soil sites. Although treatment techniques such as bioremediation, thermal desorption, soil vapor extraction, soil washing and soil flushing, bioventing, electrokinetic and phytoremediation have been demonstrated to be potential techniques [4-7]; yet none of the above – mentioned soil remediation techniques have categorically been selected as universal. Nonetheless, electrokinetic techniques have attracted increased interests in the last decade due to demonstrated promising laboratory and pilot-scale experiments that led to attractive field implementations, particularly in soil with low permeability [4, 5, 8, 9]. The most distinct advantages of electrokinetic technique is its in-situ applicability to both saturated and unsaturated soils that render it a versatile technology for remediation of wide range of contaminated soils under varying subsurface conditions.

2.1 Electrokinetic Treatment of Contaminated Sites

The cost effectiveness, relatively low energy consumption [10] and ability to remove mixture of different pollutants of the electrokinetic technique has shown great promising potential of it in-situ soil remediation, and has attracted lots of increasing attention among engineers and government officials in the last decade. This could be as result of promising bench-scale and pilot-scale experiments that yielded encouraging results in some fields [8, 10-13]. Electrokinetic process is the introduction of direct current electric fields to a contaminated soil-water system via electrodes placed in it which initiate several mechanisms which act independently or synergistically to induce mobilization of water and other species (contaminant) in solution. Although it has shown some promising lab and pilot scale results, its effectiveness may be retarded by various factors ranging from type of soil, adsorption and desorption of contaminant on the soil surface, and polarization due to hydrogen and oxygen gas generated at the electrodes [11, 12]. Various techniques on enhancing electrokinetic have been developed to tackle these retarding factors and improve the efficiency of the technique [12].

Figure 2.1 shows a typical electrokinetic remediation system. Electrodes are inserted into the subsurface and a direct current applied which induces the movement of contaminants towards the electrodes of opposite charge. The electrodes conditioning solutions are then pumped out and treated.

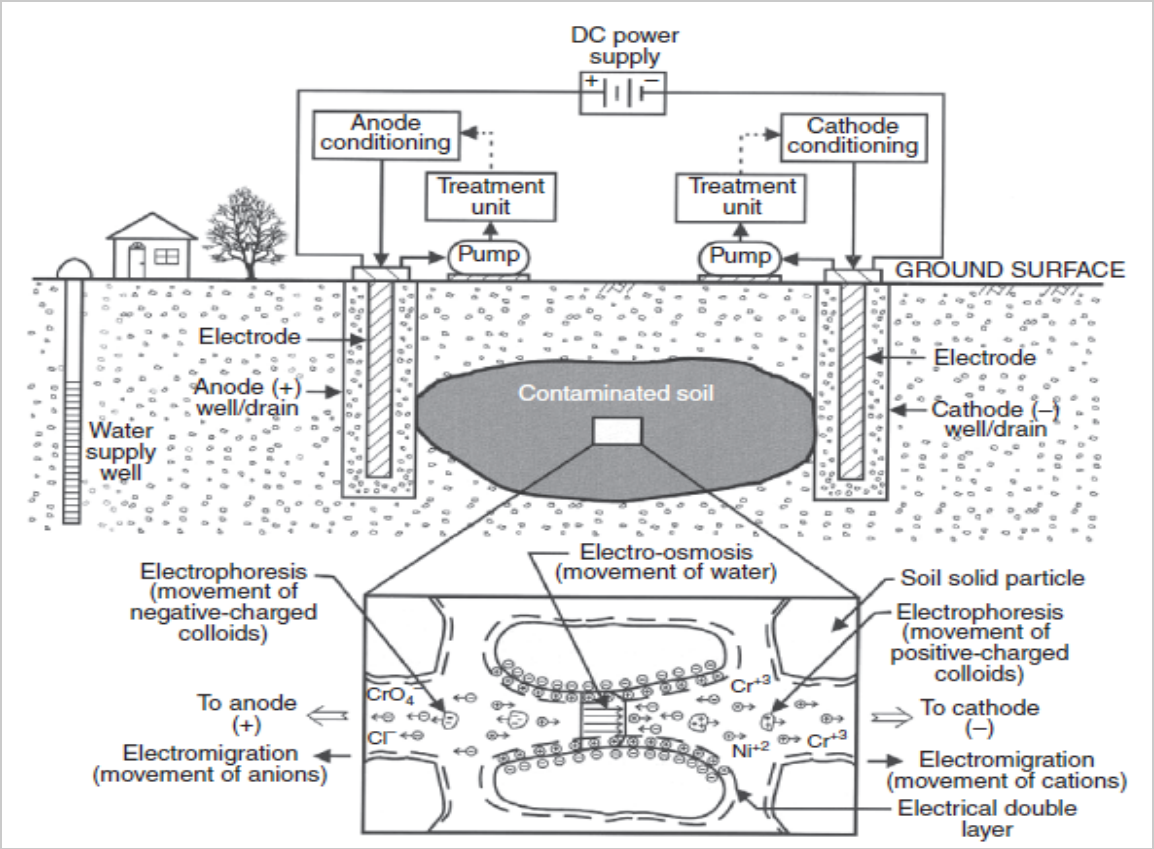


Figure 2.1: Electrochemical remediation schematics: Krishna, R. et al (2009)

2.2 Electrokinetic Remediation Principles

Electrokinetic process is conventionally achieved by applying DC electric fields to contaminated soil-water system via electrodes placed in it which induces variations to the hydrological properties of soil due to concurrent physicochemical reactions taking place [1]. As result, the migration of subsurface contaminants is imposed mainly, via three known mechanisms:

2.2.1 Electroosmosis

Electro-osmosis is the movement of soil water or groundwater from anode to the cathode under hydraulic gradient and induced electric gradient. But the hydraulic gradient

contribution is negligible in low permeability soils (low hydraulic conductivity e.g clayey soils).

Electroosmotic flow velocity according to Helmholtz-Smoluchwski theory is given as:

$$\boldsymbol{v_{eo} = -\frac{D\zeta}{\eta} E_Z} \quad \textbf{2.1}$$

Where: (ζ) Zeta potential, (E_z)Applied voltage gradient, (η) fluid viscosity and (D) dielectric Constant.

The electroosmotic permeability coefficient which is a function of zeta potential controls the rate of electroosmotic flow. Several researchers found it to range between 4.91×10^{-06} to 1.57×10^{-05} $cm^2s^{-1}v^{-1}$ [14]. The zeta potential is a function of clay mineral, ionic species, pH, and ionic strength.

2.2.2 Electro-migration

Electro-migration is the movement of ions and ion complexes towards the electrode of opposite charge, the induced movement resulting from electromigration is superimposed to that resulting from electroosmosis thereby complementing each other. Electromigration is independent of the permeability of soil as such will remove contaminant from all type of soil.

Extent of electromigration of a given ion depends on soil porosity, applied potential gradient, pH gradient, initial concentration, presence of competitive ions and soil conductivity. Electromigrative velocity is given by:

$$\boldsymbol{v_{em} = u_i z_i n \tau F E} \quad \textbf{2.2}$$

Where:/u_i/ is ion mobility, /z_i/ is ionic valence, /n/ is porosity, /Ƭ/ is Tortuosity, /F/ is faraday and /E/ is electric field strength.

The ionic mobility of which defined as the velocity ionic specie as a result of unit electric filed is estimated by Nernst-Einstein-Townsend relation:

$$\boldsymbol{u_i = \frac{D_i|z_i|\mathrm{F}}{\mathrm{R}T}} \qquad \textbf{2.3}$$

Where: /D/ is diffusion coefficient, /R/ is general gas constant and /T/ is Kelvin temperature.

2.2.3 Electrophoresis

Electrophoresis is the transport of charged particles of colloids to the opposite charge electrode, mass transport through this mechanism is negligible in low-permeable soil compared to electromigration and electroosmosis. However it is significant in soil suspension [11, 15].

The dominant and most important electron transfer reactions that occur at electrodes during the electrokinetic process is the decomposition of water to produce oxygen and hydrogen ions at the anode; while at the cathode, hydrogen gas and hydroxyl ion are generated as below:

At the anode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

At the cathode: $4H_2O + 4e \longrightarrow H_2 + 4OH^+$

The hydrogen ions produced at the anode decrease the pH near the anode and the generated acid front is carried towards the cathode by electrical migration, diffusion and advection. At the same time, an increase in the hydroxide ion concentration causes an

increase in the pH near the cathode. Non-ionic species such as most organic contaminants are transported along with the electroosmotic induced water flow; while contaminants bound to mobile particulate matter can be transported via electrophoresis and metals or charged ions are transported mainly by electromigration [1, 11, 16]. The direction and quantity of contaminant movement is influenced by the contaminant concentration solubility and hydrophobicity, soil type and structure, and the mobility of contaminant ions, as well as the interfacial chemistry and the conductivity of the soil pore water [17]. The removal efficiency generally depends on the nature of the contaminants, and soil properties, such as pH, permeability, adsorption capacity, buffering capacity, etc [18]. Moreover, other interacting mechanisms such advection that is generated by electroosmotic flow and externally applied hydraulic gradient, diffusion of the acid front to the cathode, and the rate of migration of cations and anions towards the respective electrode also significantly influence the efficiency of the electrokinetic process [19]. Once the target contaminants are successfully transported to the electrodes, they may be removed by electroplating, precipitation co-precipitation, pumping near the electrode or complexing with ion exchange resins [11].

2.3 Environmental Significance of Heavy Metals

"Heavy metals" is a collective term which applies to the group of metals and metalloids with atomic density greater than 4000 kgm^{-3}, or 5 times more than water [20]. They are known to be natural components of the earth's crust. Although some of them act as essential micro nutrients for living beings, due to their persist nature in the environment coupled with their toxicity, they can cause damage or death in animals, humans, and

plants even at trace levels [21, 22]. The most toxic forms of these metals in their ionic species are the most stable oxidation states e.g. Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+} in which, they react with the body's bio-molecules to form extremely stable biotoxic compounds which are difficult to dissociate [23]. Due to increased industrial activities and modernization, heavy metal pollution has gradually become one of the major concerns of environmentalist due to their susceptibility long-term source of pollution to groundwater and the ecosystem.

2.4 Electrokinetics Remediation of Heavy Metals Contaminated Sites

Electrokinetic technologies have demonstrated viability of effective remediation of soils and groundwater contaminated with heavy metals, such as Cu, Zn, Pb, Cd, Cr, Ni, Hg, As, Co, Sr, radionuclide's U [11, 12, 24-27]. It is reported by many researchers [11, 28], the that heavy metals ions in the soil are attracted by static electricity forces possessed by the negatively charged colloids. This attraction depends on the electronegativity of the soil and the dissociation energy of the ions [29]. With a suitable Soil pH conditions, the heavy metals may undergo sorption either by adsorption mechanism or by ion exchange. The desorption of ions is highly essential in the electrokinetic technique and it depends on the following on the soil's pH, surface density of clay minerals, type of cations and its concentration and the amount of carbonates and organic matter in the soil. It have been observed during the electrokinetic experiments that the current density decreases as the process progresses, this current decrease might be attributed to the following [11, 28]:

Activation polarization: the hydrogen and oxygen gas bubbles generated at the electrodes during the electrokinetic process cover up the electrodes thereby insulating and reducing the electrical conductivity.

Resistance polarization: is the white layer majorly of insoluble salts and impurities found during or after the electrokinetic process at the cathode which inhibits the conductivity and ultimately reduces the current density.

Concentration polarization: the hydrogen ions formed at the anode and the hydroxyl ions at the cathode are attracted towards the electrode of opposite charge thereby reducing the current and ultimately the electroosmotic flow. It may therefore be concluded that the soil containing mixed heavy metals contaminants affect the conductivity and so also the interaction between the contaminants. It is also worth noting that the electrokinetic technique as most of the soil remediation techniques can only extract mobile contaminants from soil [30, 31], and knowing that contaminants can exist as sorbed species on soil particles, solid species as precipitate, sorbed species on colloidal suspension in pore fluid or dissolved species on soil pore fluid. Only contaminants that exist either in dissolved form or sorbed on suspended colloidal particles in soil pore fluid can be extracted by electrokinetic and most other remediation technologies [12]. It is therefore important to use enhancement techniques to increase solubility of complexes formed, solubilize contaminants in soil and keep them in a mobile state so as to increase removal efficiency and reduce current consumption by depolarization of the electrodes [11, 12, 28].
In many instances, coupling electrokinetic with other remediation techniques has

proven very much an effective enhancement as the synergy can achieve results that are better than the individual results sum up together.

2.5 Techniques to Enhance Electrokinetic Remediation of Heavy Metals Contaminated Soil

Enhancement techniques in electrokinetic remediation of heavy metals contaminated soils are used so as to create a favorable environment for effective contaminant removal and overcome its limitations. This is achieved through keeping contaminants in soils in a soluble and mobile state, controlling the soil pH within favorable values for electrokinetic application and the use of electrokinetic coupled with other techniques to provide synergistic remediation. In that regards, the enhancement techniques are grouped according to their type of enhancement [12].

2.5.1 Contaminant Solubilization

Some contaminants in soils may exist in sorbed form on soil particles or as precipitates depending on the subsurface condition, thus making them in an immobile state. This state of immobility may bring retardation in the migration of contaminant and ultimately reduce the remediation efficiency [11]. In other to solublize and make thess contaminants mobile, enhancement agents are used to achieve that as the process progresses, these includes: complexing agents, chelating agent, surfactants, cosolvents and solutions containing cation.

Chelating agents

Chelants are usually organic compounds capable of desorbing metals from the surface of soil particles through formation of complexes that dissolves in water and then remove to electrokinetic remediation. The chelation process is formation of two or more separate bonds between a multi-bonded and single bonded ligand. Figure 2.2 shows the steps through which a biodegradable chelantethylenediamine-N,N-disuccinic acid (EDDS), is use to enhance electrokinetic removal of Pb from soil particles surface. This is achieved through a four step process as illustrated in the figure; injection of chelants, formation of Pb-EDDS complex, desorption of the complex from the soil surface and extraction of the Pb-EDDS complex through electromigration or electroosmosis [12]. Yeung and Gu [32] have reviewed the use of chelating agents in electrokinetic remediation of contaminated soil and found that the most used are aminopolycarboxylates including diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA), and hydroxycarxylates such as citric acid.

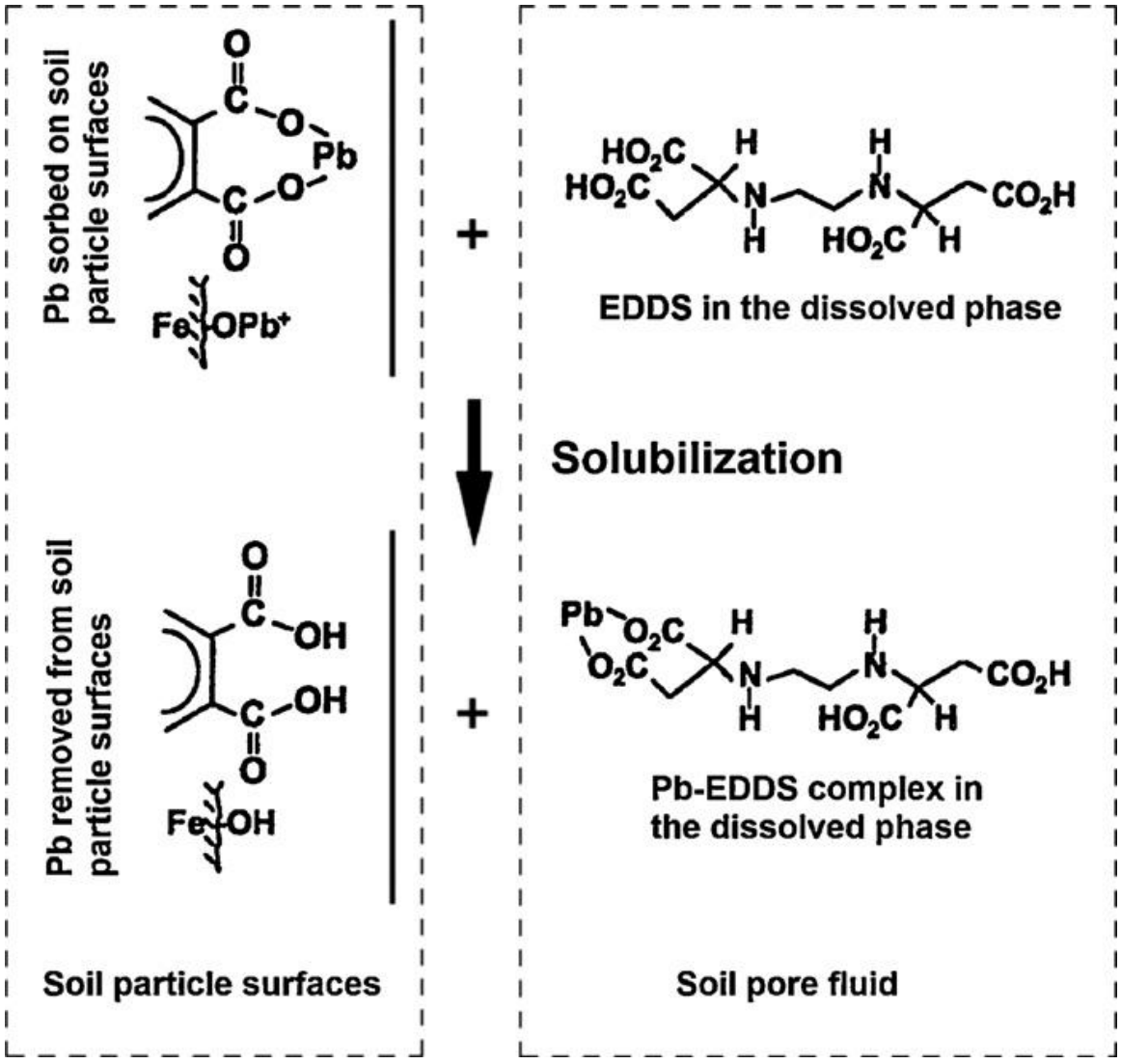


Figure 2.2: Removal of Pb from soil particle surface using EDDS as chelant [33].

Niinae*et al* [33] uses EDDS, EDTA and Citric acid as chelating agents in enhancing the electrokinetic remediation of lead contaminated soil with EDTA having the best results at ambient temperature and having more than 80% lead removal at pH 4, 7 and 10. EDDS is the next to 80% lead removal at both pH 7 and 10, and less than 40% at pH 4. Citric was found to be least maximum removal of 50% at pH 4, about 20% at pH 7 and almost zero at pH 10. Another study by Zhang *et al* [34] was conducted where the combination of

EDTA and citric acid was used a good result of lead removal was obtained with an average efficiency of 83.3%.

Gu *et al* [35] studied Citric acid industrial wastewater (CAIW) as an enhancement agent for remediating cadmium contaminated soil, and a removal 84.7% of cadmium was achieved within 514 hours of treatment. The CAIW is cheap compared to other chelating agents making it a promising enhancement agent. Chelants in addition to solubilization of contaminants also lowers the zeta potential of soil particles leading to increase in positive electroosmotic flow anode to cathode with ultimate increase in contaminant removal by electroosmosis [36]. Major limitation of the chelant enhanced electrokinectic technique is the treatment of the extracted fluid which is rich in metal-chelant complexes; this is because chelants like EDTA are toxic in particularly in their free states and poorly degradable using both physic-chemical and biological means [37-39]. Lestan *et al* [40] reviewed some methods on treating the extracted fluids to recover the chelants and found that the methods are suitable for only selected heavy metals. Thus implying more techniques for recovering chelants from used extracted fluid need to be explored to make chelant enhanced electrokinetic remediation more viable.

Complexingagents

Chemicals that generate complexes coordination with metal ions are referred to as complexing agents. The complexing agents are used as conditioning solutions (acids or bases) during the electrokinetic process. They form metal complexes that dissolve in aqueous solution. Example of the complexing agents are OH^-, I^- and NH_3^- and the examples of metal complexes formed are $[HgI_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Zn(OH)_4]^{2-}$,

$[Cr(OH)_4]^-$, and $[Cr(OH)_3]^{2-}$. Cox D. C. *et al* [41] studied the electrokinetic remediation of mercury using I_2/I^-lixiviantcomplexing agent and form HgI_4^{2-} complex. This negative complex migrated to the anode and a Hg removal of up to 99% was found to be achieved. Various other [42-44] researchers also corroborated the finding that mercury is efficiently removed from contaminated soil using iodide-enhanced electrokinetic technique as soluble complex HgI_4^2.However, Reddy *et al* [44] studied soil types; kaolin and glacial till and found kaolin with 1V/cm and 0.1M KI to give 97% mercury removal and glacial till gives lower Hg removal of 56% even at higher voltage gradient and potassium iodide concentration of 1.5V/cm and 0.2M KI. This low removal is attributed to the presence of Carbonate and organic matter in the glacial till. A study by Hakansson *et al* [45] shows that an iodide-enhanced electrokinetic remediation of mercury contaminated soil combined with sulphate reducing bacteria (SRF) is a viable technique for remediating both the soil and the extracted fluids. This iodide/iodine complexing agent is responsible mobilizing mercury which is then treated by electrokinetic; a Hg removal of more than 99% was achieved. The sulphate reducing bacteria was then able to treat the extracted fluids which is rich in Hg to a removal of over 94%.

Another complexing agent that is used by a number of researchers [46, 47], to enhance electrokinetic remediation of heavy metals is acetic acid (CH_3COOH). It has the ability to neutralize the product of water electrolysis at the cathode and maintain pH of the electrolyte within the range favorable for continuous remediation. The advantages it has over others are buffer capacity, biodegradable, relatively cheap and harmless to the environment. In another study by Zhou *et al* [48], lactic acid as a complexing agent was used to enhance the removal copper by electrokinectic. A study by Chen *et al* [49], uses

ammonium acetate (CH_3COONH_4) the complexing agent in the Cu contaminated soil at a bench scale level. It was found that the removal efficiency Cu increases as the concentration of the ammonium acetate increases from 0.1M to 0.5M. A high pH condition around the cathode observed help increase the solubility and hence increase removal rate of ammonium-copper complex.

Surfactants and cosolvents

Surfactants are compounds or ionic substances capable of lowering surface tension between a solid and a liquid or between liquids. They may also serve as wetting agents, de-emulsifiers, foaming agents, dispersants and detergents. Two types of surfactants exist; synthetic and natural surfactants. The natural surfactants (biosurfactants) are produced biologically from either yeast or bacteria which are found in different types of substrates including sugars and wastes [50]. The vast majority of surfactant studied by researchers [51-54], shows significant enhancement in remediating soil contaminated by organic contaminants. However, few researchers have tested some surfactants in enhancing the electrokinetic remediation of heavy metals contaminated soil and have proven to be effective [55]. In the general, the efficiency of using surfactant in enhancing the electrokinetic remediation of heavy metals contaminated soil is having mixed results; this is because some researchers [56, 57], reported promising results while others had reported the enhancement to be insignificant [58, 59].

The mixture of the main solvent and a small amount of a supporting solvent called cosolvent, greatly enhance the electrokinetic remediation of contaminated soil. This is due to the synergistic effect offered by the combination but it has been limited to organic

compounds and have insignificant or zero enhancement on electrokinetic remediation of heavy metals contaminated soils [12].

Solutions containing cations

Solutions containing cations have been tested by researchers in enhancing the electrokinetic remediation of heavy metals contaminated soil. Coletta *et al* [60], studied synthetic solutions containing Ca^{2+}, Na^{+} and Al^{3+} at varying concentration combined with natural solutions containing clay extract. This combined solution was used as anodic flushing solution to study its effectiveness in enhancing electrokinetic remediation of Pb contaminated soil. The cations contained in the solution proved to enhance the remediation as their concentrations increase. An optimum ionic strength of 0.001M for each element was found to give the highest Pb removal. In another study by Reddy *et al* [61], it shows that electrokinetic remediation of soil contaminated with Cr(VI), Cu(II) and Ni(II) is enhanced by Using 0.1M EDTA as catholyte and 0.1NaCl as anolyte with a voltage gradient of 1V/cm. The findings show that electroosmotic flow was maintained due to NaCl. The a removal of up to 82% was achieved for Cr(VI). The maximum removal efficiency of Ni(II) was found as to be 48% and that of Cd(II) as 26%. The removal efficiency of Ni(II) and Cd(II) were found to be low as a result of high pH soil environment leading to precipitation and accumulation around the anode.

2.5.2 Controlling soil pH

The electrochemical dissociation of electrolyte at the cathode and anode produce $OH^{-}$and H^{+} ions respectively. These ions subsequently move into the soil as a result of electric field induced as such raises the soil pH near the cathode and lowers the soil pH near the

anode. This change in soil pH may result in metal precipitation within the soil, slow down of electroosmotic flow, and impacting on the electrode materials by polarization and ultimately reduces the heavy metals removal efficiency [11, 12]. The main aim of purpose of conditioning is to keep the pH of both electrolytes within the range of value suitable for electrokinetic remediation; this range in most cases is lower for catholyte and higher for anolyte. Soil with low buffering capacity requires electrode conditioning the most. This is due to their low resistance to pH change [62]. Two methods are the most used conditioning techniques for enhancing electrokinetic remediation of metals contaminated soil which are electrode conditioning and ion exchange membranes.

Electrode conditioning

Electrode conditioning is the use of acids which may be strong or weak to neutralize the OH^- ions at produced at the cathode and the use of a base which may be strong or weak also to neutralize the H^+ produced at the anode during the electrochemical dissociation of water. It is however recommended to avoid the use of conditioning solution that may poses health hazards to the groundwater like HCl [12].

Hicks and Tondorf [63] studied the electrokinetic remediation of Zn-contaminated kaolinite soil of low buffering capacity from Georgia and where able to achieve 95% Zn removal efficiency. Their findings portrays that the isoelectric problems face could be neutralizing the high pH usually noticed at the cathode through the use of acid conditioning solution at the cathode. Many other researchers [62, 64,65], have found that conditioning the cathode with CH_3COOH has led to prevention of basic conditions in the soil, hence prevent precipitation and solubilization thereby ultimately enhancing metals

removal efficiency. A study by Lee and Yang [66], has shown that circulation of electrolyte between the electrodes could control the pH variation and prevent precipitation of heavy metals as well. In another study by Zhou *et al* [67], electrokinetic remediation of Cu and Zn low pH contaminated soil where experiments with and without conditioning electrolyte were carried out. The findings reveal the experiment carried out without conditioning led to accumulation of Cu and Zn precipitates near cathode while using lactic acid as the conditioning solution enhances the extraction efficiency of both metal contaminants from the soil. Gidarakos and Giannis [68], in an experiment performed uses CH_3COOH and Citric acid as conditioning solution to enhance the remediation of cadmium contaminated soil and found that controlling the pH increase desorption rate of Cd from surface of soil particle thereby increasing its removal by electrokinetic.

Ryu *et al* [25], uses HNO_3 and NaOH as catholyte and anolyte conditioning solutions to enhance the electrokinetic remediation of soil contaminated with Cu, As and Pb. These conditioning solutions were found increase to a maximum removal efficiency of 60.1%, 43.1% and 75.1% for Cu, As and Pb respectively. Cu and Pb removal enhanced by HNO_3 and As removal enhanced by NaOH. Genc *et al* [69], studied the electrokinetic remediation of sediment contaminated with Mn, Zn, Cu and Pb with CH_3COOH as a conditioning solution to both the cathode and anode, this results in pH values less 4 and as such reverse osmosis prevails thus leading poor remediation of 18%, 20% and 12% respectively for Mn, Cu and Pb. Zn was found to have zero removal in all test carried out.

Ion exchange membrane as a soil pH control

Ion exchange membrane is use to exclude specific ions from passing through it. The generated ions at the electrodes usually migrate into the soil thereby changing the soil's pH which in most cases do not favors the removal of heavy metals; this is due to the precipitation of the metal contaminants at high pH. A cation exchange membrane allows the passage of only cations through it and as such, it is placed between the contaminated soil and the cathode compartment to exclude OH^- ions produced at the cathode from entering the soil. This prevents the precipitation of metals in the soil and ultimately increases the heavy metals removal efficiency. The metals that pass through the membrane end up precipitating with the OH^- in the cathode process fluid or on the membrane surface. The deposition of the precipitates on the membrane has been the major challenge of this enhancing technique as it causes membrane fouling and reduction in membrane efficiency [12, 70, 71]. The use of membrane as an ion excluding agent in a study by Rosand *et al* [64], to enhance the electrokinetic remediation of Pb contaminated marine clay did not give any significant improvement. While in another study by Puppala *et al* [62], they use Nafion ion exchange membrane to exclude OH^- ions from moving into the soil during electrokinetic remediation of Pb contaminated illitic deposit. This membrane offers an advantage of neutralizing the catholyte without addition of any acid thus saving the cost in terms of acid but the resistance of the membrane increases the energy cost. The result portrays Nafion membrane as promising enhancement agent for electrokinectic remediation of heavy metals contaminated soil. Cation selective membrane has been used by Li et al [72], to exclude OH^- from moving into the soil so as to enhance remediation of Cu contaminated soil. The results shows that the membrane do

not allow all Cu to pass through it and also allows some OH^- passed to the contaminated soil thereby precipitating some Cu within the soil and ultimately reducing the remediation efficiency. Kim *et al* [16], uses both a cation and anoin exchange membranes as enhancement agents for improving electrokinetic remediation of Cd and Pb contaminated kaolin soil. Here, the problem of membrane fouling was taken care of by introducing an auxiliary solution cell between the Cation exchange membrane and the contaminated kaolin soil. OH^- find their way into the solution cell via small holes made on the membrane and the precipitation takes place there in the auxiliary solution compartment. Their findings shows that the removal efficiencies of both Cd and Pb were highly using the ion exchange membrane enhanced electrokinetic remediation technique. This is especially due to the presence of the auxiliary solution cell which prevents heavy metal - hydroxide precipitation in the soil.

2.5.3 Coupling electrokinetic with other remediation techniques.

Numerous techniques exist for remediating both organics and heavy metals contaminated soils. Each of them has its merits and demerits. They all can achieve certain percentage of remediation of contaminants alone and some if coupled can achieve a better remedial efficiency due to their combine effect [15, 31,73]. Amongst the technologies that have been explored to enhance remediation of contaminated soils through coupling with electrokinetics are Bioremediation, Permeable reactor barriers, Oxidation/reduction, Phytoremediation and Ultrasonication. While these technologies have been studied by numerous researchers and scientist [11, 12], other potential coupling techniques that will enhance electrokinetic are yet to be explored.

Electrokinetic-Oxidation/reduction

The oxidation/reduction remediation techniques are used to improve remediation of contaminated soil through redox reactions [31] and the most frequently used and studied is the Fenton process which involves a catalytic reaction between hydrogen peroxide and iron(II) ions to produce OH^- radicals which are strong oxidants that oxidizes mostly organics [74]. The OH^- radicals are mostly active in aqueous form thus making it difficult to oxidize sorbed contaminants on soil surface [12, 75]. Research has shown that the use of high concentration of hydrogen peroxide produces highly reactive oxidants like hydroperoxyl radicals, superoxide anaions and hydroperoxide anions that aggressively react and oxidize the sorbed contaminants [76-79]. Fenton processes in majority of cases has shown significant improvement when coupled with electrokinetic to treat organics contaminated soil but has low or non promising results with heavy metals [12]. Reddy and his co-researchers [80] applied electrokinetic-Fenton process to remediate Ni and phenanthrene contaminated kaolin at initial concentration of 500mg/kg each. A H_2O_2 concentration range of 5% to 30% was used and catalyst utilized is the indigenous soil iron for the Fenton process at a voltage gradient of 1V/cm for four weeks and at the end 56% of the phenanthrene was able to be oxidize at the highest concentration of H_2O_2 used. The Ni was found to precipitate near the anode due to high pH observed. It is concluded by enhancing the removal efficiency of both Ni and phenanthrene has be improved through optimization of the concentration of the oxidants/catalyst, voltage gradient and control of the pH. Reddy and Chinthamreddy [81], in another study investigated the electromigrative behavior of Cr(VI), Ni(II), and Cd(II) in two different types of soil; kaolin and glacial till, the behavior of the metal contaminants where

investigated with and without reducing agents. Voltage gradient of 1V/cm was applied for about 9 days. Cr(VI) was found to reduce completely to Cr(III) before electrokinetic remediation begins and this reduction is found to be dependent on the amount and the nature of the reducing agents. Cr(VI) was noticed to migrate less in both soils due to low pH environment making sorption on the soil surface than migration. Ni(II) and Cd(II) have significant migration towards cathode in kaolin but the high pH of the glacial till made Ni(II) and Cd(II) precipitate limiting their migration even in the presence of reducing agents. Weeks and Pamukcu [82], introduced Fe^{2+} reducing agent to a Cr^{6+} contaminated soil. This reducing agent has shown that Cr^{6+} could be successfully reduced to Cr^{3+} by electrokinetics making the two techniques coupled together more effective.

Electro-Bioremediation

The use of microorganism (bacteria) to decompose, oxidize or transform hazardous contaminants into benign or less harmful forms is considered as bioremediation [15]. The success of bioremediation depends on the availability of microorganisms, food (contaminants) and nutrients. This is difficult in most cases of low hydraulic conductivity clays or soils. Electro-bioremediation is a coupled technology whereby the electrokinetic provides all the requirement for the bacteria by electrokinetic flow mechanisms [83]. Electroosmosis has been the major mechanism used for injecting bacteria into the contaminated soils to be remediated. Most of the successful electro-bioremediations were implemented on soils contaminated by organic compounds [84-86]. A study by Lee et al [87], indicates how the injection of Acidithiobacillusthiooxidans (sulfur oxidizing bacteria) into soil contaminated with Zn, As, Cu, Cd, Pb and Co enhanced the electrokinetic remediation technique.

Electrokinetic/Permeable reactive barrier

Reactive materials placed between contaminated soil and the electrode compartment which traps or treat the contaminants before reaching the electrode compartments are regarded as Permeable reactive barriers(PRBs). Lots of these PRBs have gained attention by researchers and scientist in recent years [12]. Amongst the PRBs used are lasagna process and zero-valent iron (ZVI).

Lasagna process

In lasagna process, a treatment zone is created between both the electrodes compartments and the contaminated soil, where treatment takes place mainly by sorption on application of electric field [88]. The contaminants migrate from soil towards the electrodes through the treatment zone where the contaminants are treated. The major advantage of this technology is its complete In situ treatment of both soil and groundwater. Among other advantages of lasagna process is the possibility of recycling the cathode effluent back to the anolyte thus neutralizing the pH of the soil environment [11]. The technology has been used to treat phenolic contaminated kaolin [88] at bench scale and TCE-contaminated soils at a number of real fields [3, 10, 89]. Ma *et al* [90], in a study investigated the remediation of 2,4-dichlorophenol and Cd contaminated soil using the lasagna process with bamboo charcoal as the sorbed material at different polarity reversal rates. Their findings portray lasagna as an effective technology in the simultaneous removal of both the contaminants. Lukman [91], studied the lasagna process and investigated the effect of voltage gradient, polarity reversal and initial contaminants concentration on the simultaneous removal efficiency of Cu, Zn, Cd, Cr, Pb, Hg, phenol

and kerosene spiked on a local Saudi Arabia soil. The sorption material used in his study was activated carbon produced locally from date pits. The study models various responses

Zero-ValentIron(ZVI) PRB

Weng et al [92], studied ZVI PRB barrier in the electrokinetic remediation of Cr^{6+}-contaminated clay. The PRB was made of granular ZVI and sand at a ratio of 1:1 by weight. The findings of their investigation shows H^{+} ions migration was highly slowed down due to the migration of CrO_4^{2-} ions in opposite direction leading to a reverse electroosmosis. High concentration of Cr^{6+} found in the anolyte and Cr^{3+} precipitate found in the catholyte signifies high Cr removal. Cr^{6+} reduction to Cr^{3+} was found to increase due to ZVI PRB. Another study by Cang et al [93], also investigated the use of electrokinetic/ZVI PRB to decontaminate Cr-contaminated a removal of up 72% Cr removal was achieved which is much higher the that of the electrokinetic alone.

Electrokinetic/Phytoremediation

The use of specific plants to treat or remediate soils and groundwater contaminated with both organic and inorganic contaminants is termed as phytoremediation [31]. The slow movement of the contaminants to roots and shoots of the used plants has been one of the major challenges of the contaminants. Therefore coupling phytoremediation with electrokinetic helps solves the slow movement of contaminants challenge through electrokinetic processes; electromigration, electroosmosis and electrophoresis [15]. O'Connor *et al* [94], studied the coupled electrokinetic/phytoremediation to treat a soils contaminated with Cu, Cd and As. The result shows that the electric field introduced is

responsible for moving the contaminants towards cathode. Parts of the contaminants are being taken up to the roots and shoots of the perennial ryegrass grown within the contaminated soil near the cathode. Indian mustard was grown in a soil contaminated with Pb at a bench-scale by Lim *et al* [95], EDTA was added to the soil and electric field applied. The EDTA was meant to dissolve the Pb soil and migrated by electric field which then would be absorb by the shoots system. The Pb concentration on the shoots was noticed to be about four times that of EDTA addition alone. The use of ryegrass phytoremediation to EDTA and EDDS enhanced electrokinetic remediation of Cu contaminated soil also improves it by 46% than using EDTA alone and by 61% than using EDDS alone [96]. Aboughalma *et al* [97], in a bench scale study uses the tubers of potato to remediate Zn, Cd, Cu and Pb contaminated soil by using three conditions; no electric field, a dc electric field and an ac electric field. Their results shows that the contaminants concentration found in the plants roots is in the sequence of increasing order; ac electric field > dc electric field > no electric field. Another study by Cang et al [98] also corroborated the fact that the rate of plants roots uptake of heavy metals from a contaminated soil is highly increase by the coupled electrokinetic/phytoremediation technique and emphasis on the voltage gradient being the most significant factor affecting the plant growth and metal uptake into the roots and shoots systems.

Electrokinetic/Ultrasonication

The use of high frequency sound waves (>20kHz) or energy to improve contaminants removal in a contaminated soil is termed Ultrasonic remediation. The Ultrasonication improves remediation by increasing the kinetic energy of the soil fluid, decreasing soil fluid viscosity leading to increase in electroosmotic speed and increase in porosity [99].

The electrokinetic/ultrasonic technology used by Chung and Kamon [99] to remediate phenanthrene and Pb contaminated soil has proven to increase the remedial efficiency from 85% and 88% using electrokinetic alone to 90% and 91% for phenanthrene and Pb respectively. Similar improvement was noticed when remediating a soil contaminated by Cd and diesel fuel from 75% and 67% to 83% and 87% respectively.

From the reviewed literature so far, it can concluded that electrokinetic remediation with appropriate enhancing agent or coupled with other techniques has proven to be a promising technology for remediation of groundwater and soil contaminated with different types of heavy metals existing either alone or in mixed form. However, one of the major challenges still limiting its application is the long period of time (thereby consuming huge amount of energy) to ensure its effectiveness and success. Hence, in order to improve the effectiveness of EKR and reduce remediation time towards removing heavy metals from the groundwater and soils, significant efforts have been dissipated via exploring more strategies to achieve that. Some of these strategies include, applications of sinusoidal electric fields or polarity reversal [100-102] pulsed voltage [26, 103].

Ryu *et al* [103], investigated the feasibility of pulsing the electric field in the electrokinetic remediation of abandoned agricultural land contaminated with Zn and Cd. Their findings shows similar removal efficiency was obtained at half energy consumption of the non pulsed electric field. This implies pulsed electrokinetic technique as economically viable for treating heavy metal contaminated soils. Ryu *et al* [26], in another study vary the pulse frequency, pulse time ratio and applied voltage using the one factor at a time method and found that high pulse frequency and and higher voltage

increases the heavy metals removal efficiency also affirming the cost effectiveness of the enhancement technology. These studies by Ryu *et al* [26, 103], succeeded in increasing the removal of heavy metals from the soil surface with decreased polarization and electrical energy consumption. Rojo and Hensen have reported that pulsed electric field improved the effectiveness of electro-dialytic remediation for removing copper from mine tailings [104]. Rojo *et al* [101], study the effect of sinusoidal electric field and polarity reversal in the remediation of copper mine tailings and found an improvement of 70% in the removal of Cu on the use of sinusoidal field at the same condition with which a conventional dc electric field is applied. High voltage was observed to increase energy consumption and a 24hr polarity was found to increase removal efficiency. Rojo *et al* [105], improves the previous study by introducing pulsing, the short period of pulsing time(off time in milliseconds) periodically favors the electrokinetic remediation due to depolarization that occurs during the pulse time and with a further reduction in energy consumption. Moreover, Reddy and Saichek [106] found that application of periodic electric potential increased phenanthrene solubilisation and mass transfer. In addition, Kornilovich *et al* [107] reported that pulsed voltage system led to similar removal efficiency compared to constant system but provide noticeable electrical energy savings due to pause Time. The findings of a study by Tian and Lisbeth [108] on pulsed electrodialytic remediation of Cu and As contaminated soil; shows an energy saving of up to 67% was achieved and a maximum removal of 54% and 30% were achieved for Cu and As respectively. A trial to replace cation exchange membrane by a filter paper was found to drastically decrease the energy consumption but this in turn decrease the heavy metals removal efficiencies [109].

A continuous transport of contaminants in electrokinetic remediation depends on the electric field applied, contaminants mobility and soil surface potential (excess negative charge in soil) [11, 110]. Study on charge densities for different soil types gives the following order of increasing charge density as follows: sand < silt < kaolinite < illite < montmorillonite (bentonite). The montmorillonite having the highest charge density is expected to have a better result in terms of contaminants removal efficiency. However, studies by Virkutyte *et al* [11] shows the clayey sand and kaolinite with humic substances to have better removal efficiency than the montmorillonite. Reddy *et al* [111], studied the effect of glacial till, kaolin and Na-montmorillonite soils on electrokinetic removal of chromium. Their finding shows that a high pH value leads to low adsorption on the soil surface which ultimately favors the removal by electrokinetic. A study by Leland and Gwen [112], shows change resistance of montmorillonite's zeta potential over a pH range of 2-10 and this increase in pH was found to increase the negativity of the soil surface. Lukman [91] in a study reported that in a preliminary test of EKR for 4 days with bentonite soil, which is made of 100% montmorillonite has shown significant effect in the removal efficiency than in the use of clay with no montmorillonite. The behavior of the montmorillonite found in different studies carried out as reviewed above led to the interest in testing different percentages of bentonite so as to investigate the effect of it amount in the overall contaminants removal efficiencies and the energy consumption of the electrokinetic process.

2.6 Process Modeling and Optimization using Response Surface Methodology (RSM)

RSM as a statistical and mathematical tool has been used for modeling and optimization of various processes because of its advantages of; giving huge amount of information from few carefully designed experimental runs, simultaneous evaluation of multiple independent factors and their effect on a given response and simultaneous optimization of multiple parameters. [113-115]. RSM comprises usually of three major stages; 1) Experimental Design, 2) Response Surface Modeling and 3) optimization [115, 116]. The basic understanding of the science behind any process is the fundamental for successful utilization of RSM to design experiments, model and optimize any system or process. Bezerra *et al*. [114] reviewed various types of designs utilized by RSM and found Box-Bekhen Design (BBD) among others the best when dealing with three factors, this is due the fact that huge amount of information is obtained from small number of experiment compared to others; Doehlert Design (DD), 3 Level Factorial Design (3FD) and Central Composite Design (CCD). Doehlert Design has an advantage over others of utilizing small number of experiments when dealing with higher number of factors but it is sometimes biased due to irritability limitation which should be avoided as much as possible [114, 117, 118]. The RSM optimization technique has also proven much more successful than one at a time factor optimization technique due incorporating ability of factors interaction which is not possible with the later [117]

CHAPTER 3

RESEARCH OBJECTIVES

The main objective of this study is to investigate the effect of voltage gradient, bentoniteandclay ratio (B/C) and pulse duty cycle (on/total current flow) on the energy consumption and simultaneous removal efficiencies of mixed-heavy metals (Cr, Cd, Cu, Hg and Pb) contaminated soil with electrokinetic technique

Specific objectives to be achieved are:

1. To study the effects of voltage gradient, bentonite and clay ratio and pulse duty cycle on the simultaneous removal of the heavy metals and energy consumption of the pulsed-electrokinetic technique.
2. To investigate the effect of the operating conditions on important parameters namely: Soil pH, electrical conductivity, moisture content, electroosmotic volume and electric current during the pulsed electrokinetic process.
3. To employ response surface methodology to model the effects of the operating conditions on the contaminant removal efficiencies and energy consumption with the aid of Design Expert Software.
4. To optimize the technique in terms of voltage gradient, bentonite and clay ratio and pulse duty cycle so as to have high removal efficiencies at low energy consumption.

CHAPTER 4

MATERIALS AND METHODS

This chapter gives the entire details of the apparatus, materials and methodology adopted in the laboratory in getting results that are used in achieving the laid down objectives.

4.1 Clay and Bentonite Characterization

The soil (clay and Bentonite) samples used throughout in the study were obtained from Al-hassa oasis and have already been characterized by lukman *et al* [119, 120] elsewhere and the characterization were done according to the American Standard Testing Materials [120]. Amongst the soil parameters of concern characterized are pH, organic matter, moisture content, electrical conductivity and surface area.

4.2 Reagents

In this study, the heavy metals solutions (100mg/l each) standards were prepared from their salts which are all analytical grade namely: copper sulfate pentahydrate ($CuSO_4.5H_2O$), potassium dichromate ($K_2Cr_2O_7$), mercury sulfate ($HgSO_4$), lead nitrate $Pb(NO_3)_2$all from BDH laboratory supply company UK and cadmium metal (fisher scientific company).

4.3 Reactor Design

The reactor used in this experiment is made of Plexiglas capable of treating 2000 to 2400cm^3 of contaminated soil. It is made of three compartments with the middle for the contaminated soil and the sides for the electrode and electrolytes as shown in figure 4.1 below. The entire reactor dimension summary is given in table 4.1.

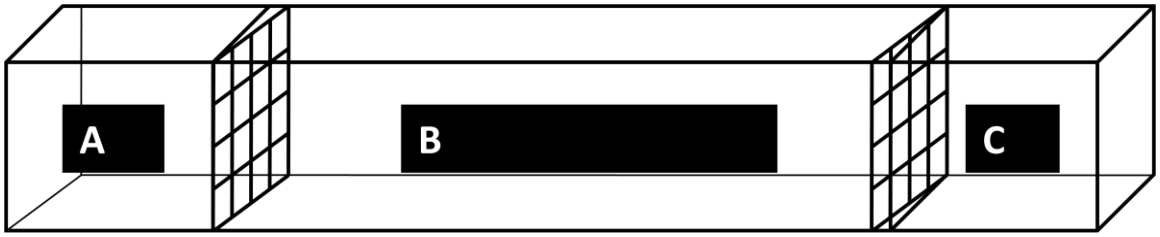


Figure 4.1: Reactor Schematic

Table 4.1: compartments and their respective dimension

Compartment	Length(cm)	Breath(cm)	Height(cm)	Capacity(cm^3)
A: Anode and Anolyte	5	10	12	600
B: Contaminated Soil	20	10	12	2400
C: Cathode and Catholyte	5	10	12	600

4.4 Experimental Design

Experiments were design using Response Surface Methodology (RSM) techniques as it offers huge information from small number of experimental runs. Box-Behnken Design (BBD) for second-order model design amongst other RSM techniques was utilized for modeling, optimization and interpretation of results because of its advantages over others which are; taking care ofcurvature (non-linear nature) of response which is beyond the capability of first order design and it is economically viable as it requires less number of experiments [115]. The statistical software used to achieve these aforementioned objectives is Design Expert Version 9 (Stat-Ease, Inc.). Thirteen Experiment were design using the BBD approach with three factors (independent variables); Voltage gradient, clay and bentonite ratio and pulse duty cycle. The software randomized the experiments to be conducted as per the BDD experimental design as depicted in Table 4.2

Table 4.2: BBD Experimental Design

Run order	Bentonite/Clay (A)	Voltage Gradient (B)	Pulse Duty Cycle (C)	Responses (Rp)				
				Rp1	Rp2	Rp3	-	Rpn
1	0.3	0.2	0.9					
2	0.3	0.6	0.5					
3	0.3	0.2	0.5					
4	0.3	0.6	0.9					
5	0.5	0.4	0.9					
6	0.1	0.6	0.7					
7	0.1	0.2	0.7					
8	0.1	0.4	0.5					
9	0.3	0.4	0.7					
10	0.1	0.4	0.9					
11	0.5	0.2	0.7					
12	0.5	0.4	0.5					
13	0.5	0.6	0.7					

4.5 Experimental Set-up

The set-up as depicted in figure 4.2 is the experimental set-up. It consists of an electrokinetic reactor made of Plexiglas filled with the mixed heavy metals contaminated soil at the middle chamber, 1N HNO_3 anolyte and 2N NaOH catholyte in the left and right chambers respectively. Two graphite electrodes (12cm × 10cm × 0.5cm each) serving as anode and cathode, a DC power supply (Sorensen SGI series), a pump (Thermo Scientific FH100) for refilling and replacing process fluids and finally the clips and connecting wires that connects the electrodes to the power source.

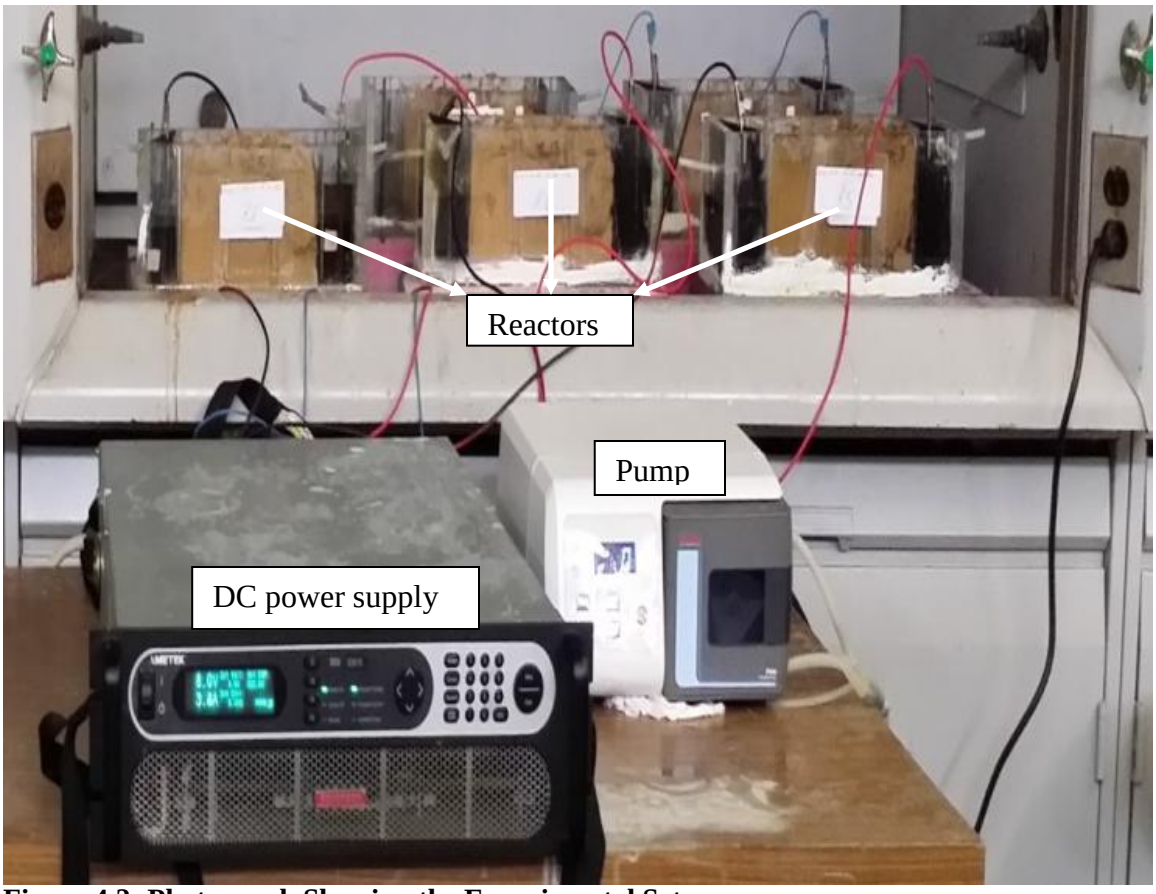


Figure 4.2: Photograph Showing the Experimental Set-up

4.6 Experimental Procedure

The soil sample of about 3 kg was spiked artificially with Cr, Cd, Cu, Pb and Hg together at an initial concentration 100 mg/l each. It was mixed very well with the help of a mechanical mixer to ensure homogeneity of the heavy metal distribution throughout the soil. The initial moisture content of the spiked soil was maintained within the range of 45-50% with the help of distilled water. The spiked soil was then carefully placed in the reactor and compacted with the help of a stainless steel spatula to minimize void space as much as possible. After the successful placing of the soil in the reactor, a porous plate and a filter paper (Whatman No 41) placed between the soil and electrolyte chambers to avoid falling of soil into the electrolyte. The 1N HNO_3 and 2N NaOH solutions for conditioning were then added to the electrolyte chambers and graphite electrodes dipped into these chambers as well which are used for generating electric field. The power supply then connected using the connecting wires (copper made) and clips. Finally the experiment was started each time with the appropriate experimental conditions (bentonite and clay ratio, voltage gradient and pulse duty cycle) according to the experimental design presented in Table 4.3. Each experiment lasts for three weeks and performed under room temperature.

Before every experiment starts, initial soil sample is taken and measures for initial soil pH, moisture content, electrical conductivity and contaminants concentrations to have a reference point. The electric current and electro-osmotic depth and electrolyte pH are parameters monitored on 12 hourly bases so as to have the variation of current with time

and for power consumption calculation, the electro-osmotic volume generated and the rate of process fluids deterioration.

At the end of each week, soil sample were drawn to measure soil pH, moisture content, electrical conductivity and contaminants concentrations remaining. The entire reactor at the end of each three weeks of each experiment is thoroughly cleaned first with tap water followed by distilled water, then with 5% HNO_3 to dissolve any hidden contaminant (heavy metal) before starting another experiment.

4.7 Analytical Procedures

4.7.1 Heavy Metals Extraction and Analysis

The detailed step by step guide lines for heavy metal extraction from soil sample is outlined in the EPA Method 3050B for acid digestion soils and that is the procedure employed in achieving the heavy metals extraction. The procedure is described summarily as follows; 2 g of soil sample is taken in duplicates, 10 ml of concentrated HCl is added to the each 2 g sample and then covered with a watch glass. It was then heated at 95ºC for 15 min, was then allowed to cool and filtered through a filter paper (Whatman No. 41). The filter paper was rinsed first with 5ml of hot concentrated HCl and then later with hot distilled water, the solution (filtrate) was finally made up to 100ml in a round bottom flask. The filtrate was then analyzed for all heavy metals using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES iCAP 600 Series, Thermo Scientific). The analysis of heavy metals using the ICP-OES was performed according the EPA Method 200.7 [121]. Linear calibration curves were developed for Cd,

Cr, Cu, Hg and Pb with correlation coefficients of 0.9999, 0.9977, 0.9991, 0.9792 and 0.9996 respectively. High purity reagents were used in developing the Curves (See Appendix for the calibration curves).

The following formula was used to compute the concentration of the heavy metals in soil (in mg/kg) from the ICP-OES results which is usually in mg/l.

Soil concentration (mg/kg) = $(C_{icp} \times V)/W$

Where:

C_{icp} = Concentration of metal in the digested sample obtained from the ICP-OES in mg/l

V = Volume of the digested soil sample in liters (0.1L in this case)

W = Wet soil sample weight utilized for digestion in kg (0.002kg in this case)

4.7.2 pH and electrical conductivity measurements.

All pH measurements both for process fluids (anolyte and catholyte) monitoring and soil samples were achieved using Jenway model 3520 ion meter whilethe soil electrical conductivity measurement were achieved for each sample at a soil to water ratio of 1:2 with the help of Accument® excel XL 30 conductivity meter (Fisher Scientific). The measurements were in mS/cm.

4.7.3 Weighing and drying

Soil samples were weighed using KERN 770 weighing balance and dried using Isotemp Oven (Fisher Scientific).

4.8 Modeling and Optimization Using Response Surface Methodology (RSM)

The responses obtained from the analyzed samples and monitored parameters; the heavy metals removal efficiencies, the power consumption, soil electrical conductivity, soil pH, and others are then modeled and the whole system optimized.

The models were generated based on the experimental results and the optimization based on the generated models. Box-Behnken Design was employed in the design of experiment (using Design Expert® Version 9.0 statistical software) with bentonite and clay ratio, voltage gradient and pulse duty cycle as independent variables.

4.8.1 Modeling procedure

For each response modeled, it was first analyzed by inserting the response values in the software. The software was then run and the models evaluated until the model falls within the acceptance criteria which are:

Step 1: P-value of less than 0.05 indicates model terms that are significant which implies acceptance of a term in a model otherwise a model will be evaluated again to remove the insignificant terms until all terms are significant.

Step 2: A reasonable R^2 (0.750-0.999), Adjusted-R^2 (Adj-R^2), Predicted-R^2 (Pred-R^2) and Adequate Precision were made sure they fall within acceptance range. A difference of less than 0.2 must be maintained between Adj-R^2 and Pred-R^2 and the Adequate precision

which measures signal to noise ratio must be greater 4 for model to be considered of acceptable quality to describe the experimental data.

Step 3: The generated models were then evaluated using the model diagnostics where the model is tested for statistical assumptions upon which parametric Analysis of variance depends. These assumptions include Normality plots, Residuals vs. Run, Predicted vs. Actual, Box-Cox and Residuals vs. Factors and in all cases, random pattern signifies a very good model.

Step 4: The generated models were finally evaluated using the model graphs where the 3D Surface plots and Perturbation plots gives a clear picture of factors variation or effects on responses and factor degree of influence.

4.8.2 Optimization procedure

The Numerical optimization was achieved by the following procedure:

Step 1: Setting goals for all the factors and responses involved in the optimization

Step 2: Inputting all lower and higher limits of factors and responses values accordingly

Step 3: The program then searches within the design space based on the models generated and select the factors combination that best meet the defined goals.

CHAPTER 5

RESULTS AND CONCLUSION

5.1 Clay and Bentonite Characterization

The soil samples collected for this study have been characterized with the results as seen for both clay and bentonite in Table 5.1.The bentonite having much higher surface area than clay which as expected as they are class with highest specific surface area [91].

Table 5.1: Physicochemical characteristics of Bentonite and Clay used in this study

Parameter	Bentonite	Clay
pH	9.53	8.3
Moisture Content, %	3.91	3.91
Soil organic matter, %	4.3	2.59
Electrical Conductivity, mS/cm	56.17	15.24
BET Specific Surface area, m^2/g	42.13	9.07

5.2 Experimental Results, Analysis and Discussion

5.2.1 Heavy Metals Removal Efficiencies

The results depicted in figures 5.1 to 5.6 shows the overall removal efficiencies of the heavy metals at the end of the three weeks of running according to the experimental design. The observed variations within each heavy metal was as a result of the of the experimental conditions while the variation between all the heavy metals depends on the nature of the soil properties and the contaminants. It can be observed from the figures that the metals with highest and lowest range of removal efficiencies are Cr and Pb ions respectively. The lowest range of Pb removal may attributed to formation of $Pb(OH)_2$ at pH values beyond 10 leading more removal by adsorption than electrokinectic [91] and this is enhanced by the bentonite percentage due to its relatively higher surface area of $42.13m^2/g$. A study by Yeung *et al*. [122] have shown that higher buffering capacity and cation exchange capacity of the soil also contributes to the low Pb ions removal and in another study by Acar *et al*. [123], a removal of 55% was achieved at 2950hours of treatment time equivalent to about 17 weeks and at an initial concentration of 5322mg/kg. The high range of removal efficiency noticed with Cr in this study is because the Cr is in the form of Cr(VI) which is highly mobile and exist as anions and easily migrate towards anode during remediation process. All this could be attributed to the fact that Chromium favors alkaline condition in soils. Cr(VI) adsorption onto soil substantially decrease with pH increase [11], and from the monitored soil pH as depicted in figure 5.6, the pH value ranges between 8.1 to 12.5 which proves the soil's alkalinity. The overall removal efficiencies of heavy metals can be observed to be decreased with increase in bentonite

ratio which may be due to the high surface of the bentonite. The increase in pulse duty cycle in all the experimental runs has been observed to increase the removal efficiencies of the heavy metals. This could be attributed to the overall increase in treatment time. The voltage gradient as one of the major factor considered in the success of electrokinetic remediation [12], has also been seen to favor the removal efficiencies of most of the metals. However, the removal efficiencies of some of the heavy metals; Cd and Cu were found to decrease with increase in the voltage gradient. This may be attributed the metals ion existing in anionic form and high current generated at due to increase in voltage may lead to high electroosmotic flow towards the cathode which opposes the anionic species migrating towards the anode [91]. Section 5.3 gives more explanation on the detail variation of the removal efficiencies taking into the account the effect of all the three factors at a time.

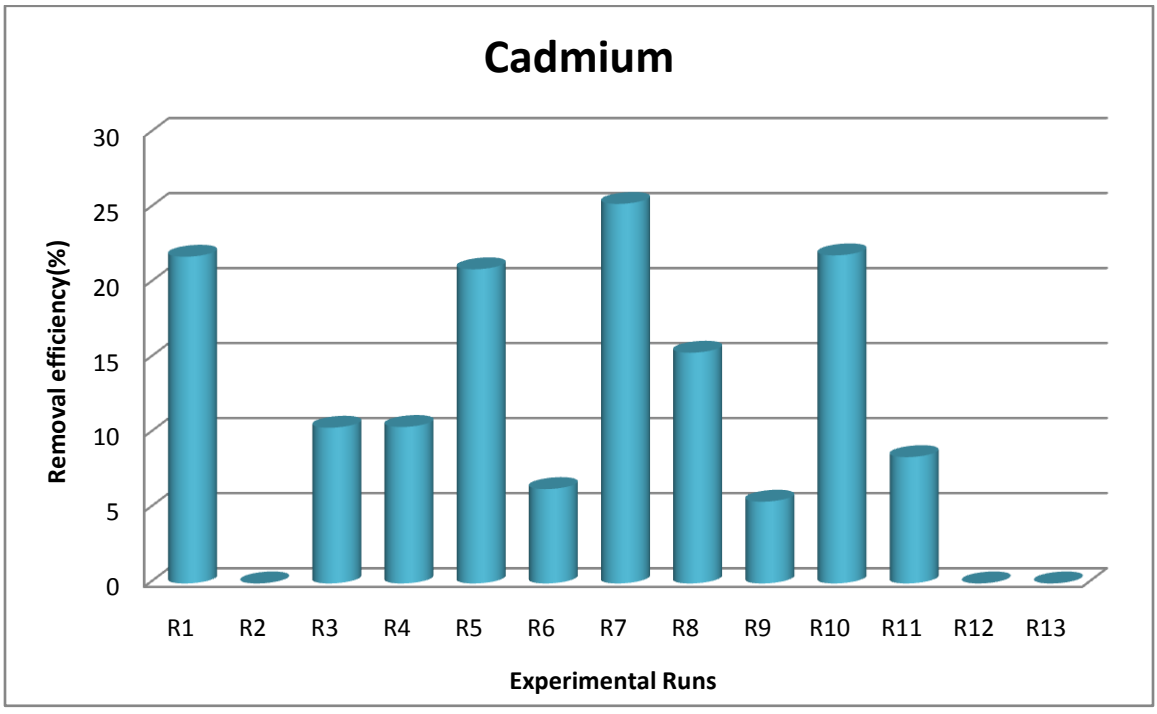


Figure 5.1: Cadmium removal efficiencies for different experimental conditions

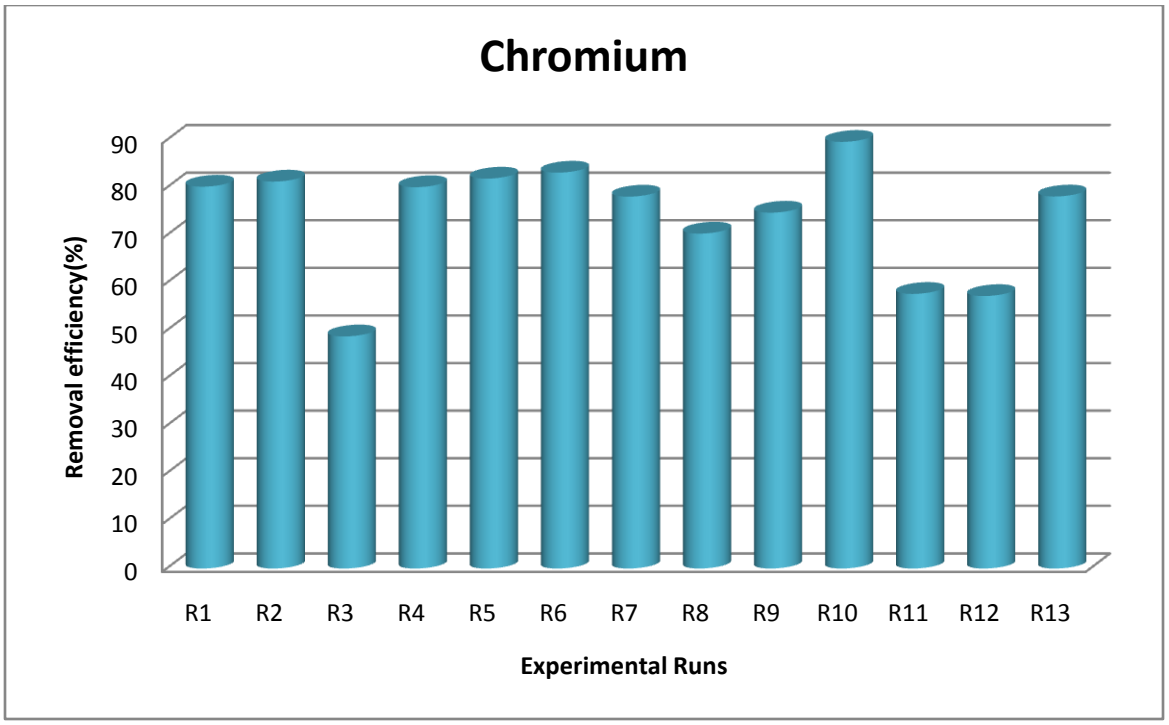


Figure 5.2: Chromium removal efficiencies for different experimental conditions

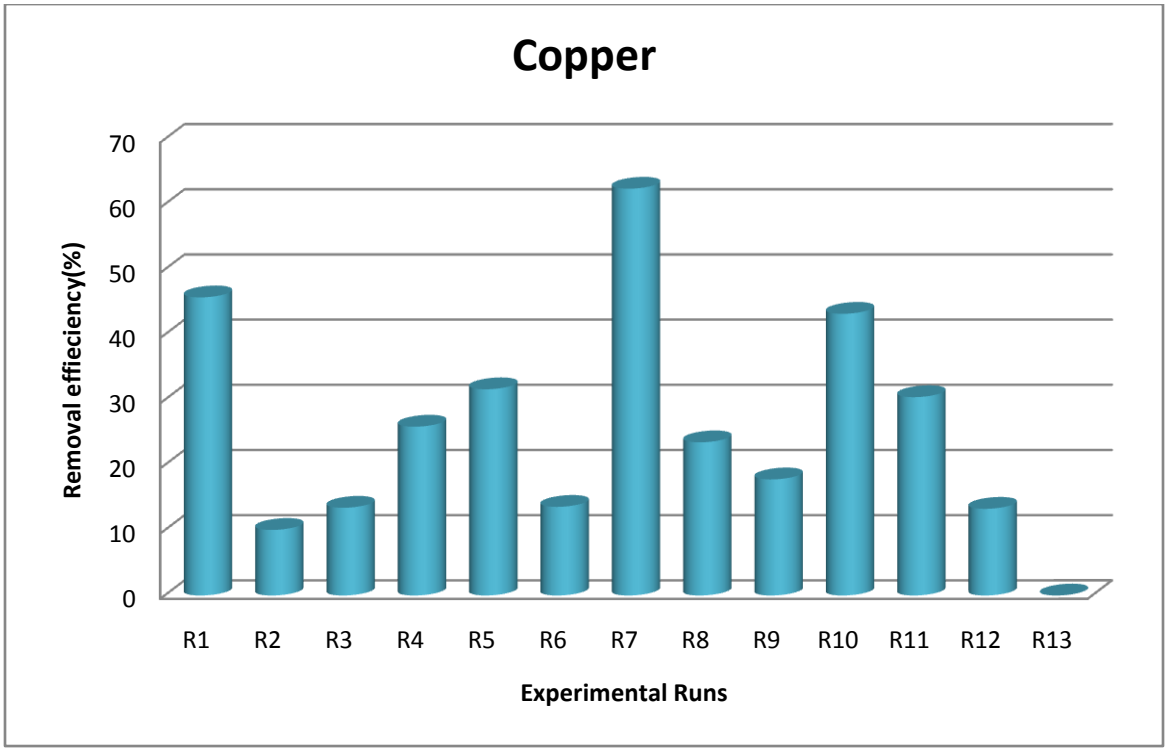


Figure 5.3: Copper removal efficiencies for different experimental conditions

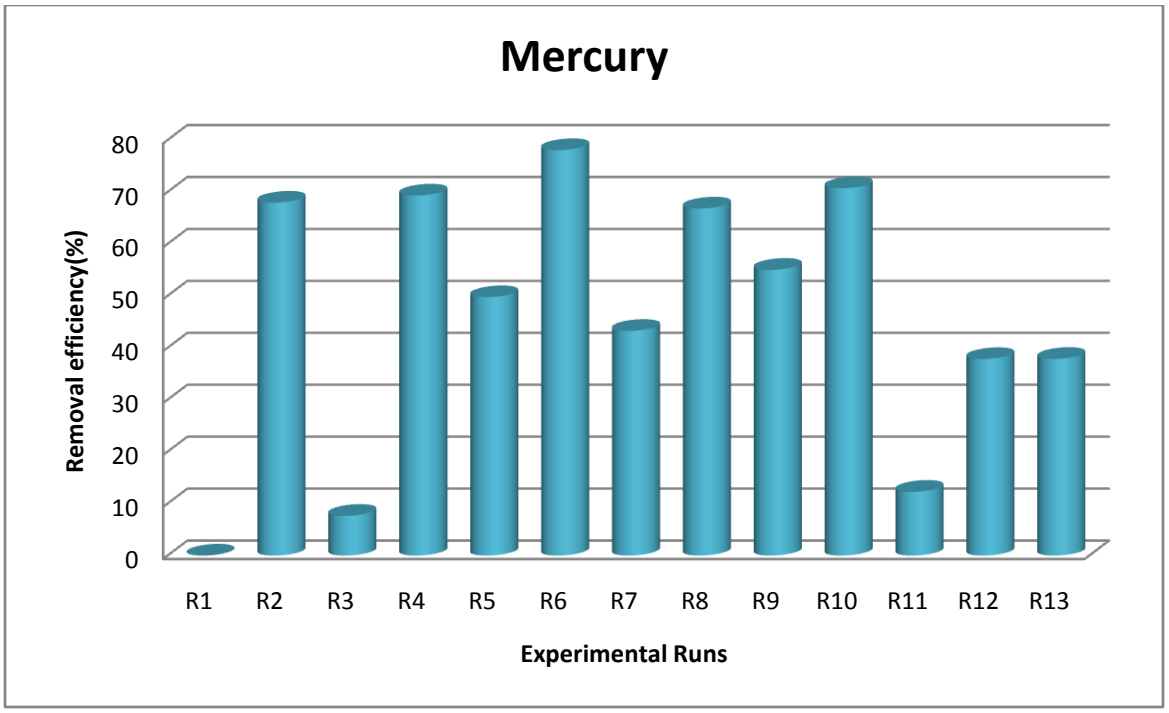


Figure 5.4: Mercury removal efficiencies for different experimental conditions

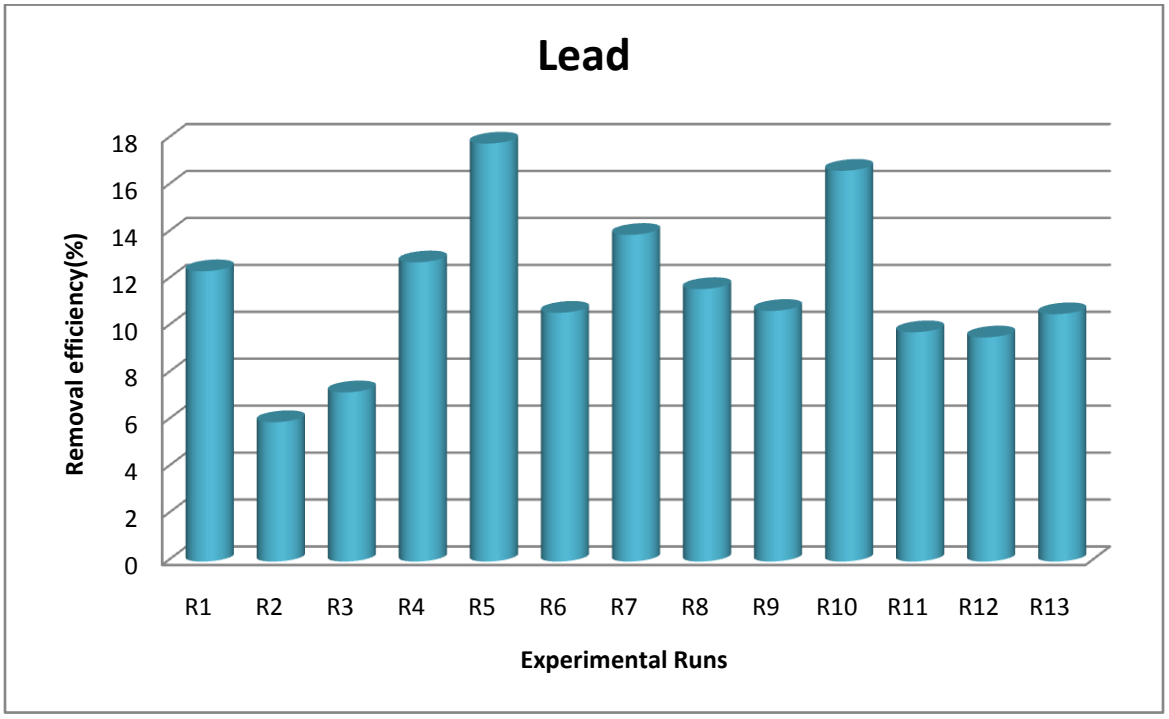


Figure 5.5: Cadmium removal efficiencies for different experimental conditions

5.2.2 Soil pH variation and control

Soil pH variation: Table 5.1 and 5.2 shows that pH of the bentonite and clay respectively as 9.0 and 8.3. This portrays the soil pH as alkaline in both cases implying that both contains appreciable soluble salts that easily hydrolyze in alkaline condition as the case with sodium carbonate [124]. This may enhances the adsorption and precipitation of heavy metals depending on the surface area and metals speciation. The soil pH variation over the three weeks of treatment time ranges from about 8.1 to 12.5 as depicted in figure 5.6 for the thirteen experimental runs. The rise in the Soil pH amongst the experimental runs may be attributed to the variation in voltage gradient as higher voltage gradient leads to increase in electrochemical decomposition of electrolyte producing more OH^- ions which migrate into the soil and hence raise the soil pH. Experimental runs R2, R4, R6 and R13 (figure 5.6) experiences the highest rise in soil pH due to their high voltage gradient of 0.6v/cm while R1, R3, R7, R11 experiences lowest rise due their low voltage gradient of 0.2v/cm. This finding is similar to a study by Lukman *et al* [125].

Soil pH control: The electrochemical decomposition of the electrolytes at cathode and anode produces OH^- and H^+ respectively. These ions migrate into the soil thereby the lowering the pH near the anode and raising the pH near the cathode [12]. In other to control the Soil pH to avoid excessive production of these ions which will retard the process, 1N HNO_3 and 2N NaOH where used continuously to neutralize the rapidly generated acid and base fronts. The overall pH rise over the 3 weeks of treatment is due to this continuous refill and replaced of the process fluids producing more of the ions raising the Soil pH. It is important to know that the high buffering capacity of the soil

may be responsible for suppressing H^+ while OH^- migrate to the soil keeping in alkaline condition [111].

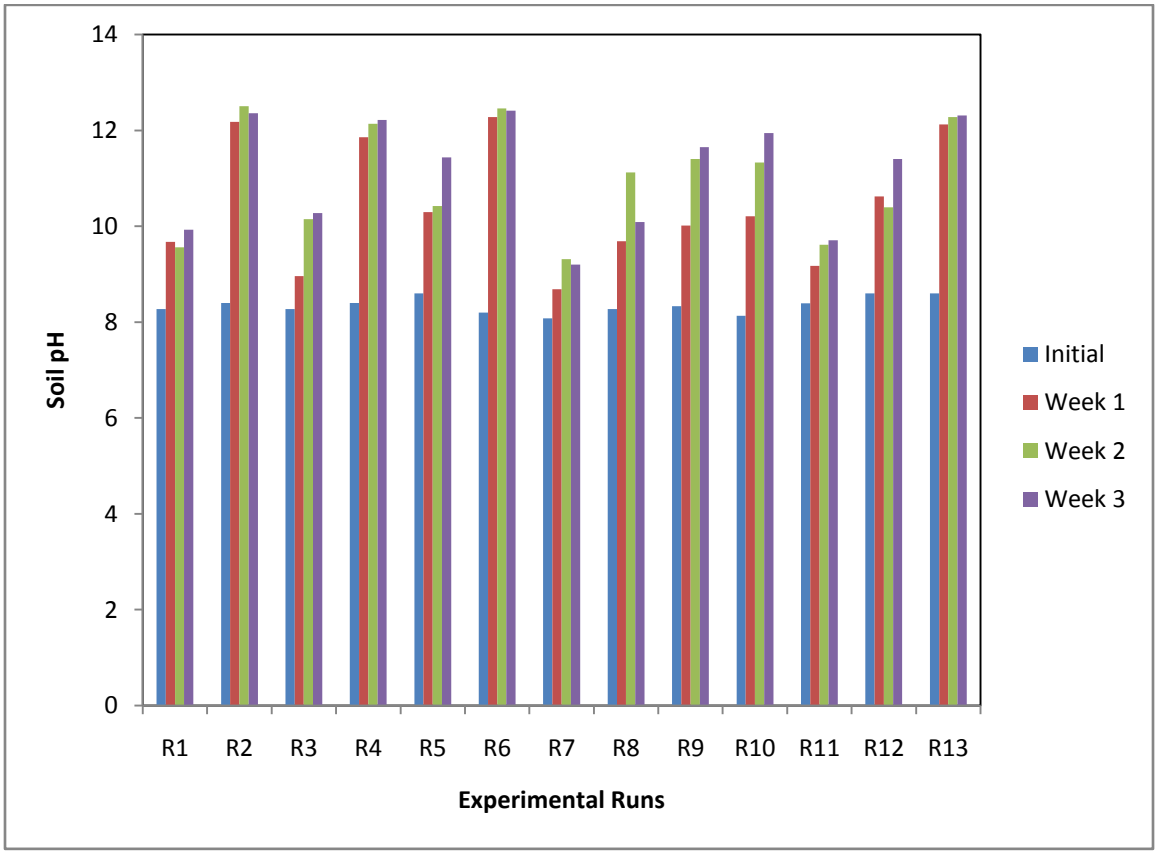


Figure 5.6: Soil pH variation with treatment time for the 13 Experimental Runs

5.2.3 Effect of treatment time on the Soil electrical conductivity

From Figure 5.7, it can be seen that for all the 13 experimental runs carried out, an increase in the electrical conductivity is observed from initial to week 3 in almost all the cases. Water is electrochemically dissociated at the anode and cathode leading to rapid production of H^+ and OH^- ions respectively as shown in equations 5.1 and 5.2, in other to neutralize these ions, a need for the use of processing fluids arises where 1 N HNO_3 and 2

N NaOH were chosen and monitored on 12 hourly bases for refill and replacement as they degrade. The process fluids electrochemically decomposes as shown in equation 5.3 and 5.4

Anode:

$$\boldsymbol{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-} \quad \textbf{5.1}$$

Cathode:

$$\boldsymbol{4H_2O(l) + 4e^- \rightarrow H_2(g) + 4OH^-(aq)} \quad \textbf{5.2}$$

Anode:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq) \quad \textbf{5.2}$$

Cathode:

$$HNO_3(l) \rightarrow H^+(aq) + NO_3^-(aq) \quad \textbf{5.4}$$

Na^+ and NO_3^- from equation 5.3 and 5.4 continuously move into the soil and migrates to the cathode and anode electrodes respectively hence leading to continous increase in the electrical conductivity as treamtment progresses [126]. This continous increase is possible because the process fluids are continously refilled and replaced as they degrade.

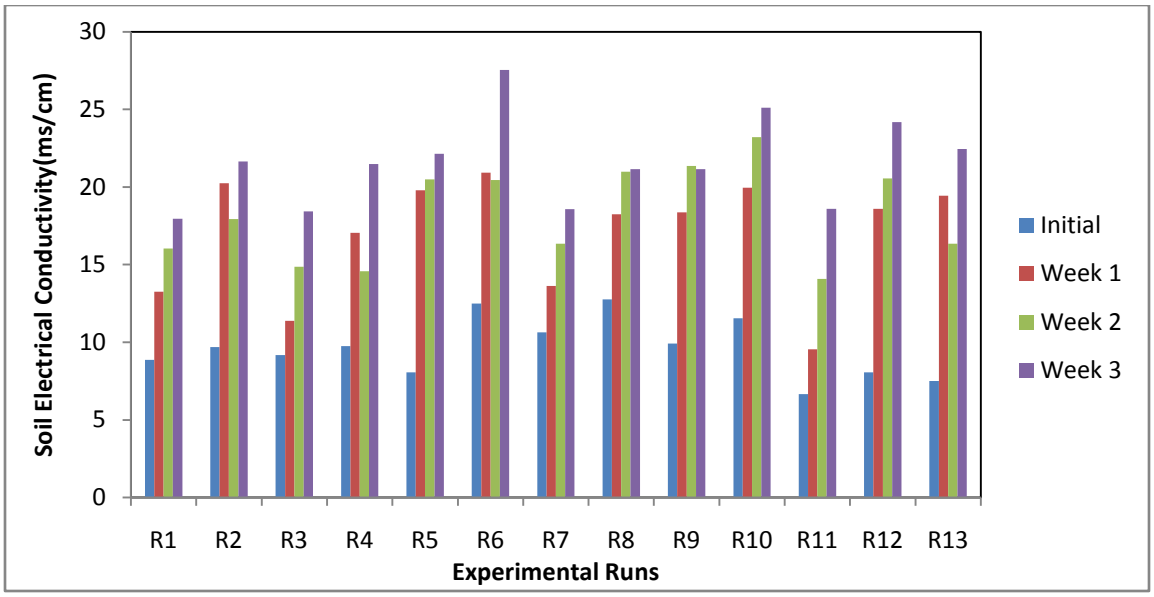


Figure 5.7: Weekly Soil Electrical Conductivity Variation

5.2.4 Soil Moisture Content

The moisture content of the soil affect electrokinetic in such a way that increase the dissolution rate of contaminants, thereby enhancing their transport by both electro-migration and electroosmosis [127, 128]. The soil moisture content was monitored throughout this study and it was found to vary less, the initial moisture content was at kept at a range of 47 to 53% and a maximum difference of 3% was recorded over the entire monitory period as depicted in figure 5.8. This maintained moisture content may be attributed the continuous refill and replacement of the degraded process fluids.

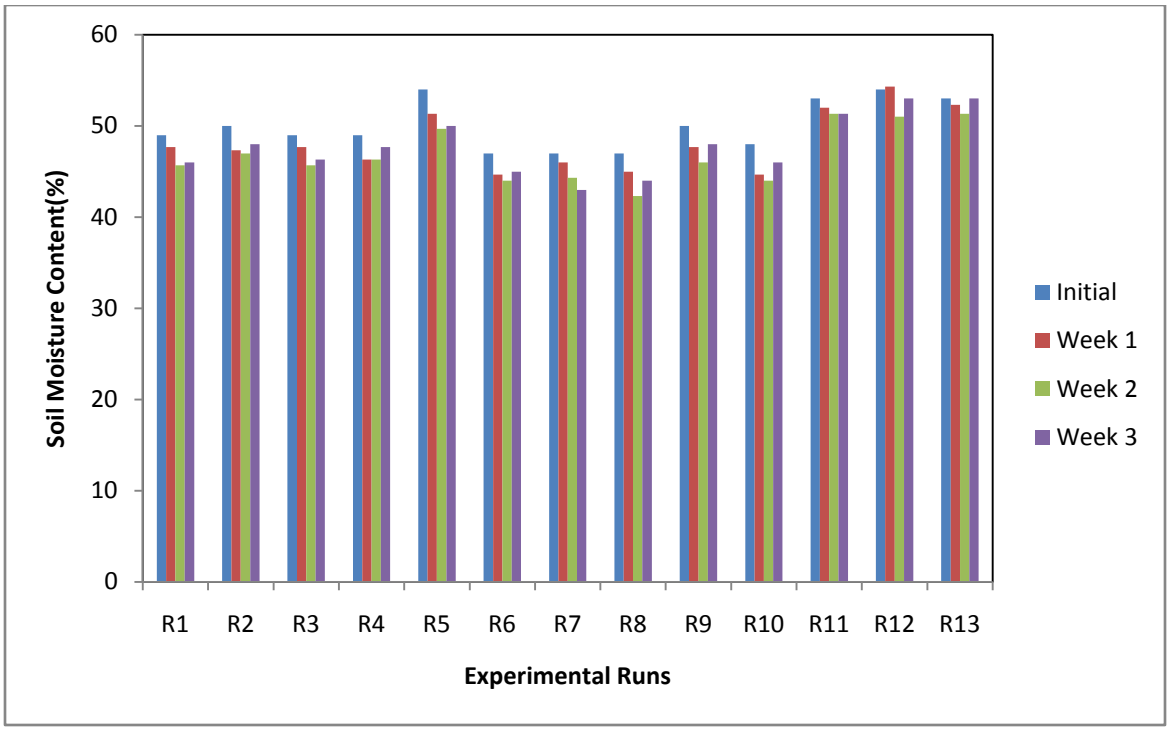


Figure 5.8: Weekly Variation of Soil Moisture Content

5.2.5 Electric Current

Figure 5.9 presents the weekly average current variation of the thirteen experimental runs for the entire duration of 3 weeks treatment time, the low current observed with R1, R3, R7, and R11 is because of the fact that they have low voltage gradient of 0.2 v/cm relative to that of R5, R8, R9, R10 and R12 with medium average current recorded due to voltage gradient of 0.4 v/cm and R2, R4, R6 and R13 with highest average current as a result of the highest voltage gradient of 0.6 v/cm applied. It is evident that the higher the voltage gradient, the more will be the quantity of current passage leading to rapid electrochemical dissociation of electrolyte with more generation of H^+ and OH^- [127, 129]. The H+ generated is neutralized by the high buffering capacity of the soil while the

OH^- ions subsequently migrate to the soil and raise the pH as observed in figure 5.6. The weekly variation of current within each experiment may be attributed to the continuous refill and replacement of degraded process fluids leading to production of more ions from the degraded fluids. These ions raise the soil electrical conductivity and subsequently the electric current [130]. However, some experiments especially those with low voltage gradient have shown a fluctuating pattern, this might be probably explained by the geochemical processes taking place within the system such as ionic dissolution, process fluids degradation and precipitation [91]. A study by Reddy *et al* [129] also found this fluctuating nature of the current. It is worth nothing that the neutralization and chemical reactions taking place at the electrodes compartments also contributes to the variation of the electric current.

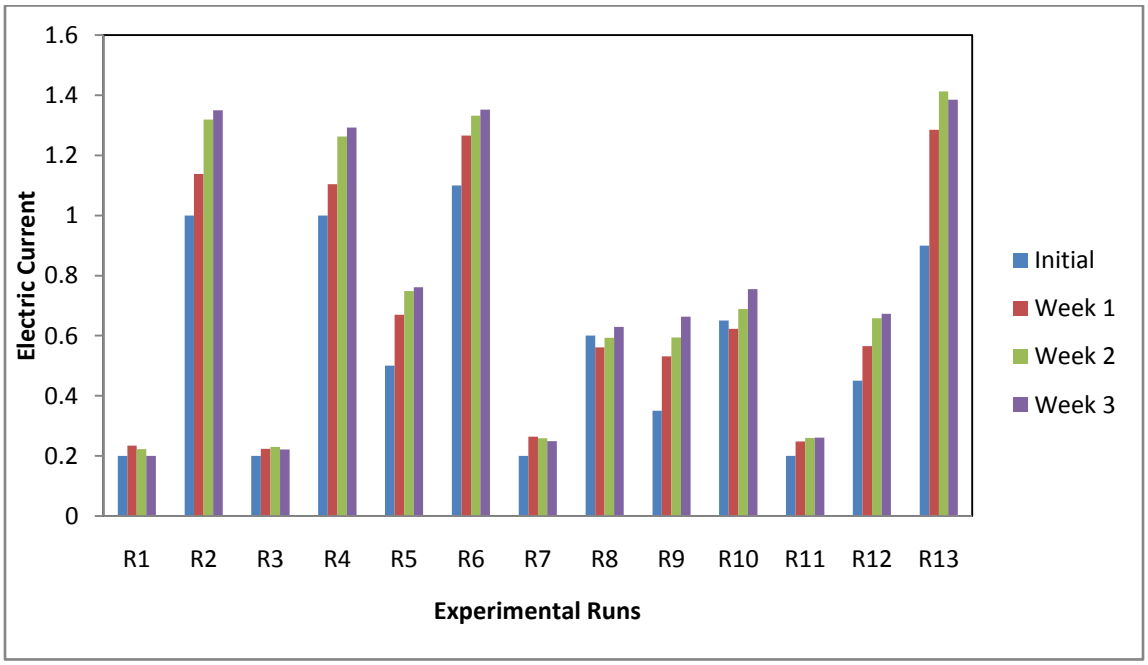


Figure 5.9: Weekly Variation of Electric Current

5.2.6 Electroosmotic Flow

The Electroosmotic volume weekly variation for each of the thirteen experimental runs is depicted in Figure 5.10. The variation of this electroosmotic flow is a function of many factors amongst which are voltage gradient, clay zeta potential, electrolyte dielectric constant and viscosity [15]. It can be clearly observe from the figure 5.7 that runs R2, R4, R6 and R13 have the highest generated electroosmotic volume which may be attributed to their high voltage gradient of 0.6 v/cm while R1, R3, R7 and R11 having the lowest due to low voltage gradient of 0.2 v/cm. The derived electroosmotic velocity according to Helmholtz –Smoluchowski (H – S) theory is given in equation 5.5 below

$$v_e = \frac{\varepsilon_s \zeta}{\eta} E = k_e E \qquad \textbf{5.3}$$

Where: v_e = electroosmotic velocity, ε_s= pore fluid permittivity, η = pore fluid viscosity,

ζ = soil zeta potential, k_e = coefficient of electroosmotic conductivity, E = voltage gradient

The electroosmotic volume monitored and measured varies due to the independent variables in equation 5.5. The electroosmotic volume normally increases with time as a result of increase in electrical conductivity of the soil with time which led to higher ionic strength as the treatment progresses [15, 91]. Reddy *et al*. [15], in a study observed that a high voltage gradient is responsible for higher electroosmotic flow due to high ionic migration leading large amount of momentum transfer to the surrounding pore-fluids. The soil zeta potential is influenced by the type of dissolved ions in the pore-fluids in addition to the electrolyte chemistry. A negative zeta potential exist with clay soils as

clays are usually negatively charged. It is important to note that zeta potential is defined as the electric potential between the mobile and fixed parts of the electrical double layer. A positive zeta potential may exist at low pH value below point of zero charge, this is because of the increase in ionic strength and protonation resulting from the more metal ions dissolved in the pore fluid and their ultimate adsorption onto the soil and the compression of the electrical double layer. The direction of the electroosmotic velocity may be reversed as a result of reversing the zeta potential. High pH deprotonates and precipitate metal hydroxides and ultimately maintains a negative zeta potential [131]. The electroosmotic flow in this study maintains a unidirectional pattern as high pH values are recorded as depicted in Figure 5.6.

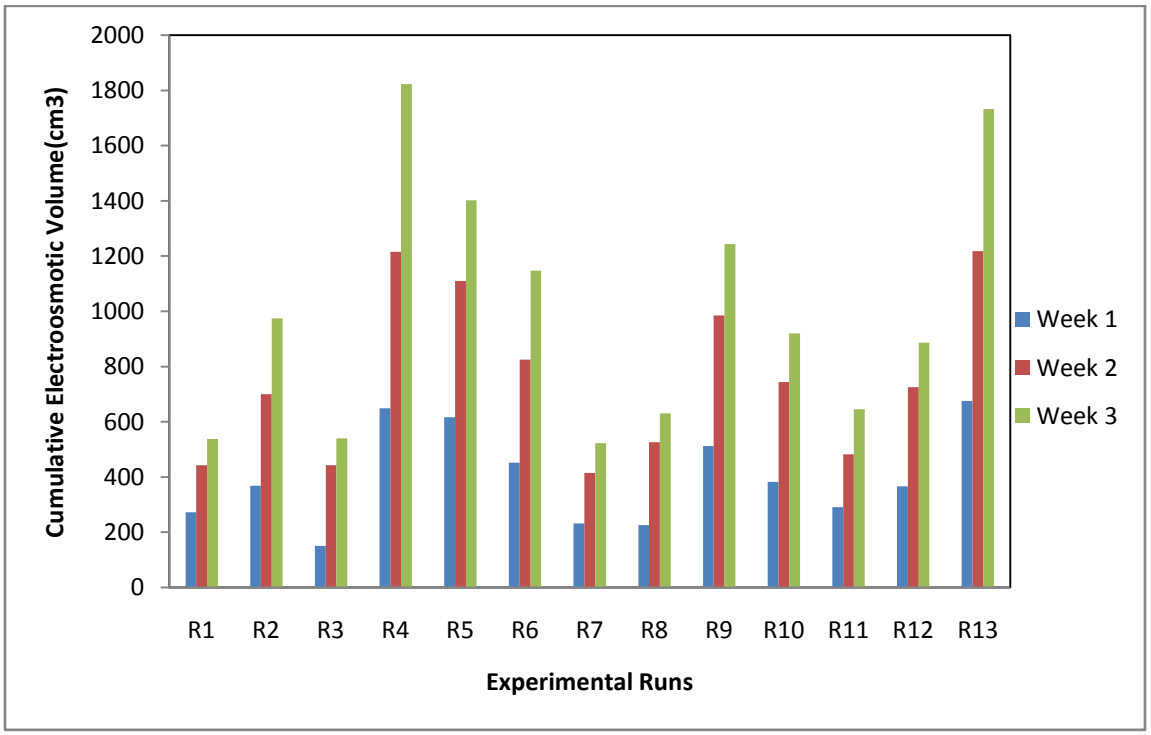


Figure 5.10: Weekly Variation of Cumulative Electroosmotic Volume for all experiments

5.2.7 Energy Consumption

Figure 5.11 presents the variation of energy consumption over the 3 weeks of treatment for the 13 experimental runs, it can be clearly observed that R1, R3, R7 and R11 has a low range energy consumption of 91.67 to 154.17 (kwh/m^3 of treated Soil), followed by R5, R8, R9, R10 and R12 with a medium range of 529.17 to 1150.00 (kwh/m^3 of treated Soil) and the last set R2, R4, R6 and R13 with the highest range of 1700.00 to 2441.67 (kwh/m^3 of treated Soil). This variation is due to the increase in voltage gradient from 0.2V/cm to 0.4V/cm to 0.6V/cm respectively for the low, medium and high range. The next factor contributing to the variation in energy consumption is the pulsing. The higher the pulse duty cycle the higher the energy consumption due to the overall increase in treatment time. The amount of bentonite has little or no effect on the energy consumption based on the experimental results. It is also worth noting that the continuous refill and replacement of the degraded process fluids introduces more ions to the soil as a result of electrochemical dissociation [91], this increase the electrical conductivity of the soil. The increase in soil electrical conductivity increases the current flow which ultimately increases the energy consumption. The 3D response surface plots in the next section gives a clear variation of these factors with energy consumption.

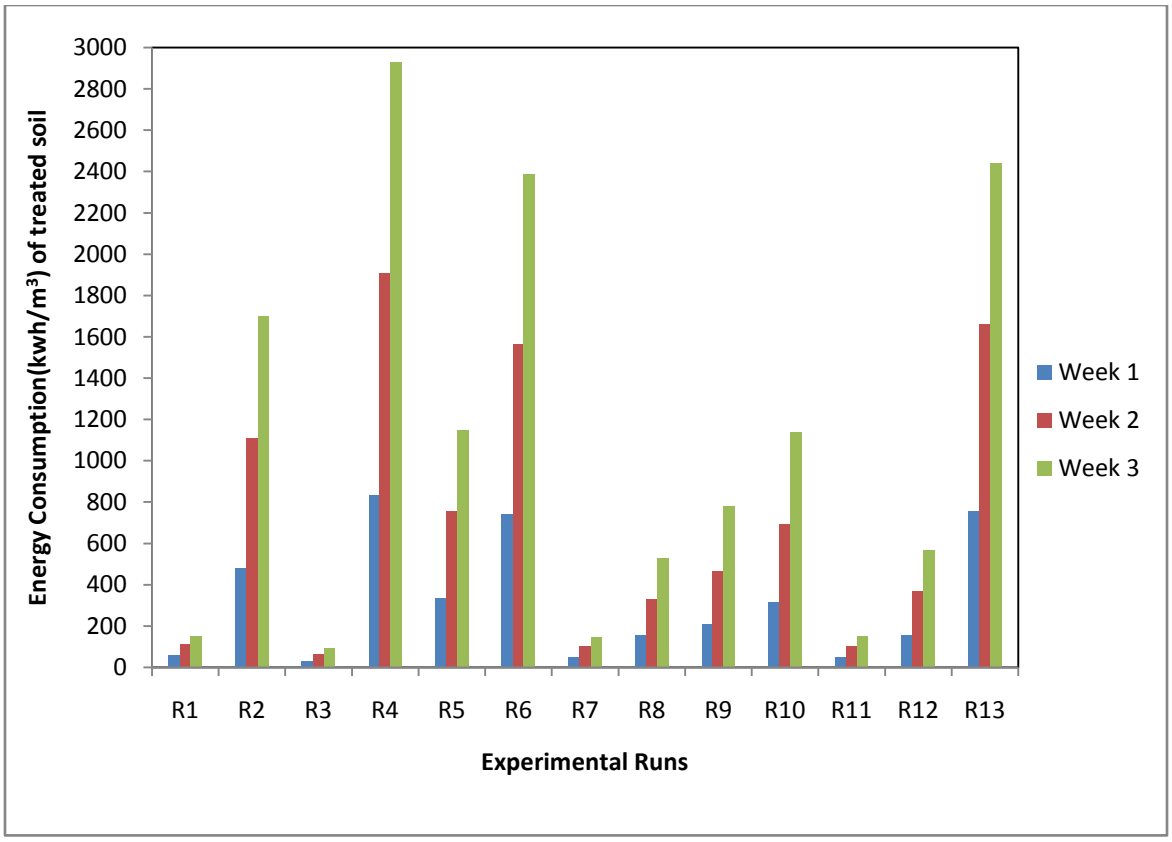


Figure 5.11: Weekly Variation of Energy consumption

5.3 RSM Modeling and Optimization of Pulsed Electrokinetic Remediation of Heavy Metals Contaminated Soil

Response surface methodology (RSM) was utilized in the modeling and optimization due to its capability of designing and optimizing processes as elucidated in the reviewed literature. Factors of concern which were used here are the voltage gradient, Bentonite and clay ratio and pulse duty cycle. The factors were varied according to the experimental design by Box Behnken Design Technique. The response surface predictive models were generated in terms of heavy metal removal efficiencies and energy

consumption. The entire modeling and optimization was carried out with the help of Design Expert Software.

5.3.1 Box Behnken Design Model's Development

The Box Behnken Design was utilized for the experimental design, modeling and optimization due to its advantage of taking care of curvature when dealing with three factors and its ability to extract huge amount of information from small number of experiment [114]. The experimental results were modeled, optimized and interpreted using the Response surface methodology with the help of Design Expert®9.0 Software (Stat-Ease, Inc.). The three independent variables (factors) modeled are coded at three levels which are low (-1), medium (0) and high (+1) as presented in Table 5.3. A total of thirteen (13) experiments were randomized by the Design expert software using the Box Behnken Design (BBD)approach. These designed experiments were carried out in the laboratory and results for heavy metals removal efficiency and energy consumption are as displayed in Table 5.4. The coding of factors was based on equation 5.2

$$x_i = \frac{X_i - \frac{\left(X_{high} + X_{low}\right)}{2}}{\frac{\left(X_{high} - X_{low}\right)}{2}} \qquad \textbf{5.4}$$

Where x_i is the new coded value, X_i is the actual value of a given variable (low, medium or high) while X_{low} and X_{high} are the low and high levels of the variable.

The RSM models fitting is explained by the following general quadratic function given in equation 5.7

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \quad \textbf{5.5}$$

Where y = response (dependent variable), β_o, β_i, β_{ii}, β_{ij} = coefficients to be fitted using regression for constant term, linear, quadratic and interaction parameters respectively, $x_i$and x_j are the coded values of the independent variables, k = number of factors and ε = statistical error term.

Table 5.2: Factor levels and codification

Factor	Symbol	Unit	Coded factor levels		
			-1	0	+1
Bentonite/Clay	A	_	0.1	0.3	0.5
Voltage Gradient	B	V/cm	0.2	0.4	0.6
Pulse duty cycle(on/total time)	C	_	0.5	0.7	0.9

Table 5.3: Experimental Design and Results for Box Behnken Design (BBD)

Runs	Factors			Responses(removal efficiencies and energy consumption)					
	B/C	V.G (V/cm)	P.D.C	Cd (%)	Cr (%)	Cu (%)	Hg (%)	Pb (%)	Energy Consumption (kwh/m^3 of treated Soil)
1	0.3	0.2	0.9	21.78	80.23	45.74	0.00	12.37	150.00
2	0.3	0.6	0.5	0.00	81.30	10.06	67.95	5.94	1700.00
3	0.3	0.2	0.5	10.38	48.77	13.46	7.65	7.21	91.67
4	0.3	0.6	0.9	10.43	80.12	25.90	69.32	12.75	2933.33
5	0.5	0.4	0.9	20.94	81.92	31.64	49.75	17.81	1150.00
6	0.1	0.6	0.7	6.29	83.18	13.60	78.06	10.60	2387.50
7	0.1	0.2	0.7	25.30	78.14	62.41	43.26	13.92	145.83
8	0.1	0.4	0.5	15.38	70.37	23.50	66.82	11.61	529.17
9	0.3	0.4	0.7	5.45	74.77	17.81	55.02	10.68	779.17
10	0.1	0.4	0.9	21.87	89.64	43.22	70.73	16.65	1141.67
11	0.5	0.2	0.7	8.42	57.70	30.43	12.28	9.77	154.17
12	0.5	0.4	0.5	0.00	57.25	13.30	37.84	9.55	566.67
13	0.5	0.6	0.7	0.00	78.17	0.00	37.87	10.54	2441.67

5.3.2 Models' Fitting and statistical analysis

The data presented in Table 5.4 is the experimental results as carried out according to the experimental design. It was supplied to the Design Expert software. The software then utilizes least square regression method in estimating the coefficients of the polynomial function for each model equation according to the experimental data. Table 5.5 to 5.12 presents the analysis of variance for all the responses modeled that included Cd removal, Cr removal, Cu removal, Hg removal, Pb removal, Energy consumption, Soil electrical conductivity and Soil pH.The response surface models developed were evaluated with all the necessary probability and statistical tests as found in the analysis of variance tables at 5% significance level. A probability value (p-value) of less than 0.05 implies a model is statistically significant in predicting a response. The models' p-values of 0.0003, 0.0001, 0.0019, 0.0021, 0.0011, 0.0001, 0.0001, and 0.0006 were arrived at for Cd removal, Cr removal, Cu removal, Hg removal, Pb removal, Energy consumption, Soil pH and Soil electrical conductivity, respectively. This implies that all the models developed are very much significant in their predictions. For each model developed, the model was looped many times to remove the insignificant terms until a final refined model is developed where all the terms were significant based on the p-value of less than 0.05. Equations 5.8 to 5.15 gives the final equations generated through fitting the experimental results to equation 5.7 and performing some regression analysis. The best fitted models obtained are reduced quadratic, reduced 2FI, simple linear, simple linear, reduced quadratic,

reduced quadratic, reduced quadratic and simple linear for the eight responses respectively.

$$\text{Cd Removal} = + 5.82 - 4.93\times A - 6.15\times B + 6.16\times C + 2.65\times AB + 3.61\times AC + 4.09\times A^2 + 4.73\times C^2 \quad (5.6)$$

$$\text{Cr Removal} = + 73.97 - 5.79\times A + 7.24\times B + 9.28\times C + 3.86\times AB - 8.16\times BC \quad (5.7)$$

$$\text{Cu Removal} = + 25.47 - 8.42\times A - 12.81\times B + 10.77\times C \quad (5.8)$$

$$\text{Hg Removal} = + 45.89 - 15.14\times A + 23.75\times B + 1.19\times C \quad (5.9)$$

$$\text{Pb Removal} = + 11.58 - 0.64\times A - 0.43\times B + 3.16\times C + 2.09\times A^2 - 2.24\times B^2 \quad (5.10)$$

$$\text{Energy Consumption} = + 1.88 + 0.033\times A + 2.67\times B + 0.75\times C + 0.70\times BC + 0.15\times A^2 + 1.05\times B^2 \quad (5.11)$$

$$\text{Soil Electrical Conductivity} = +18.99 - 0.67\times A + 3.73\times B + 0.20\times C - 3.31\times B^2 \quad (5.12)$$

$$\text{Soil pH} = +10.98 - 0.15\times A + 1.34\times B - 0.089\times C \quad (5.13)$$

Table 5.4: Analysis of variance table (ANOVA) for Cadmium removal

ANOVA for Response Surface Reduced Quadratic model (Cadmium Removal)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	965.10	7	137.87	48.04	0.0003	significant
A-Bentonite/Clay	194.80	1	194.80	67.87	0.0004	
B-V. Gradient	302.09	1	302.09	105.25	0.0002	
C-Pulse duty cycle	303.36	1	303.36	105.69	0.0001	
AB	28.04	1	28.04	9.77	0.0261	
AC	52.22	1	52.22	18.19	0.0080	
A^2	46.77	1	46.77	16.29	0.0100	
C^2	62.70	1	62.70	21.84	0.0055	
Residual	14.35	5	2.87			
Cor Total	979.45	12				

Table 5.5: Analysis of variance table (ANOVA) for Chromium removal

ANOVA for Response Surface Reduced 2FI model (Chromium Removal)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	1701.77	5	340.35	47.19	< 0.0001	significant
A-Bentonite/Clay	267.85	1	267.85	37.14	0.0005	
B-V. Gradient	419.49	1	419.49	58.17	0.0001	
C-Pulse duty cycle	688.58	1	688.58	95.48	< 0.0001	
AB	59.52	1	59.52	8.25	0.0239	
BC	266.34	1	266.34	36.93	0.0005	
Residual	50.48	7	7.21			
Cor Total	1752.25	12				

Table 5.6: Analysis of variance table (ANOVA) for Copper removal

ANOVA for Response Surface Linear model (Copper Removal)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	2808.10	3	936.03	11.59	0.0019	significant
A-Bentonite/Clay	566.98	1	566.98	7.02	0.0265	
B-V. Gradient	1312.81	1	1312.81	16.25	0.0030	
C-Pulsing	928.32	1	928.32	11.49	0.0080	
Residual	727.16	9	80.80			
Cor Total	3535.27	12				

Table 5.7: Analysis of variance table (ANOVA) for Mercury removal

ANOVA for Response Surface Linear model (Mercury Removal)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	6358.07	3	2119.36	11.22	0.0021	significant
A-Bentonite/Clay	1833.96	1	1833.96	9.71	0.0124	
B-V. Gradient	4512.76	1	4512.76	23.90	0.0009	
C-Pulsing	11.35	1	11.35	0.060	0.8118	
Residual	1699.29	9	188.81			
Cor Total	8057.37	12				

Table 5.8: Analysis of variance table (ANOVA) for lead removal

ANOVA for Response Surface Linear model (lead Removal)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	122.25	5	24.45	15.78	0.0011	
A-Bentonite/Clay	3.26	1	3.26	2.11	0.1900	
B-V. Gradient	1.47	1	1.47	0.95	0.3620	
C-Pulsing	79.84	1	79.84	51.52	0.0002	
A^2	12.28	1	12.28	7.92	0.0260	
B^2	14.11	1	14.11	9.11	0.0195	
Residual	10.85	7	1.55			
Cor Total	133.10	12				

Table 5.9: Analysis of variance table (ANOVA) for Energy consumption

ANOVA for Response Surface Reduced Quadratic model (Energy Consumption)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	66.84	6	11.14	2716.98	< 0.0001	significant
A-Bentonite/Clay	8.930E-003	1	8.930E-003	2.18	0.1905	
B-V. Gradient	57.24	1	57.24	13960.44	< 0.0001	
C-Pulsing	4.46	1	4.46	1086.81	< 0.0001	
BC	1.98	1	1.98	483.01	< 0.0001	
A^2	0.066	1	0.066	16.13	0.0070	
B^2	3.08	1	3.08	750.05	< 0.0001	
Residual	0.025	6	4.100E-003			
Cor Total	66.87	12				

Table 5.10: Analysis of variance table (ANOVA) for Soil pH

ANOVA for Response Surface Linear model (Soil pH)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	14.79	3	4.93	40.78	< 0.0001	significant
A-Bentonite/Clay	0.29	1	0.29	2.38	0.1574	
B-Voltage Gradient	14.44	1	14.44	119.43	< 0.0001	
C-Pulse duty cycle	0.063	1	0.063	0.52	0.4886	
Residual	1.09	9	0.12			
Cor Total	15.87	12				

Table 5.11: Analysis of variance table (ANOVA) for Soil Electrical Conductivity

ANOVA for Response Surface Reduced Quadratic model (Soil Electrical conductivity)						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	148.98	4	37.25	16.62	0.0006	significant
A-Bentonite/Clay	3.60	1	3.60	1.60	0.2410	
B-Voltage Gradient	111.40	1	111.40	49.70	0.0001	
C-Pulse duty cycle	0.31	1	0.31	0.14	0.7193	
B^2	33.67	1	33.67	15.02	0.0047	
Residual	17.93	8	2.24			
Cor Total	166.92	12				

The models' correlation coefficients are as presented in Table 5.13 with R^2 values of 0.9853, 0.9712, 0.7943, 0.7891, 0.9185, 0.9996, 0.8926, 0.9315 arrived at for for Cd removal, Cr removal, Cu removal, Hg removal, Pb removal, Energy consumption, Soil pH and Soil electrical conductivity models' respectively. Though R^2 is regarded as a biased [113, 117], hence a better correlation coefficient that is less biased and more accurate for evaluating model adequacy called adjusted R^2 is employed.

For instance, Cd removal model with R^2 of 0.9853 was good and reasonable agreement of less than 0.2 difference between the adjusted R^2 of 0.9648 and predicted R^2 of 0.8600 is reached ensuring absence of outlier in the data. This implies that 96.48 % (adjusted R^2) of the total variation in the Cd removal may be attributed to the experimental factors studied and about 0.5% chance that the variation of the response surface model might be due to noise (experimental error). This implies that the prediction ability of the model is within 95% confidence limit. The adequate precision which measures the signal to noise ratio was determined as 19.10 which much more than the minimum value of 4 for model adequacy, this implies an adequate signal reasonable predictions from the developed model and therefore can be used in navigating the design space. A standard deviation of 1.69 was arrived at buttressing good quality of the model. It is important to note that the standard deviation tends to a smaller value as the adjusted R^2 value tends to unity. The predicted sum of squares gives a measure of how the developed modeled fits the design points.

In a similar manner, the response surface models for Cr removal, Cu removal, Hg removal, Pb removal, Energy consumption, Soil pH and Soil electrical conductivity have good adjusted R^2 values and were in good agreement with the respective predicted R^2as

can be seen in Table 5.5. All other model adequacy tests were found to in similar nature with that of the Cd removal. All the test carried out prove the models to be of high quality and good enough to navigate the design spaces for the models thus drawing reliable inferences. Most of the models fits shows some credibility through the statistical evaluation carried out. However, Cu removal, Hg removal and Soil electrical conductivity with R^2 values of 0.7943, 0.7891 and 0.8926 may be considered low values of R^2 for good quality models. But the fact that even all other statistical evaluations prove adequate, these models can to a great extent provide behavior of response due to the factors studied [113, 117]

Table 5.12: Response Surface models correlation coefficients values for the responses

Responses	Model	Std Dev.	PRESS	R^2	Adj. R^2	Pred. R^2	Adeq. Precision
Cd Removal	Reduced Quadratic	1.69	137.16	0.9853	0.9648	0.8600	19.100
Cr Removal	2FI	2.69	201.36	0.9712	0.9506	0.8851	21.784
Cu Removal	Linear	8.99	1544.4	0.7943	0.7257	0.5631	9.459
Hg Removal	Linear	13.74	3664.7	0.7891	0.7188	0.5452	10.205
Pb Removal	Reduced Quadratic	1.24	37.45	0.9185	0.8603	0.7186	13.864
Energy Consumption	Reduced Quadratic	0.064	0.17	0.9996	0.9993	0.9974	145.624
Soil Electrical Conductivity	Reduced Quadratic	1.5	48.01	0.8926	0.8388	0.7124	9.482
Soil pH	Linear	0.35	2.21	0.9315	0.9086	0.8607	15.897

5.3.3 RSM Models Diagnostics and Validations

The models developed were statistically tested and have proven to be adequate for their respective predictions of the responses as the function of the factors under study. This section checks the models for the statistical assumptions upon which the parametric analysis of variance (ANOVA) depends, and also validate the model's accuracy in terms of experimental values (Actual) and predicted values. Figure 5.12, 5.13, 5.14, 5.15, 5.16, 5.17, 5.18, and 5.19 present the plots for the models assumptions and validation for Cr removal, Cu removal, Hg removal, Pb removal, Energy consumption, Soil pH and Soil electrical conductivity models' respectively. The sub-Figures a, b, c and din the Figures 5.12 to 5.19 represents the plots of constant error assumption, normality assumption, model validation and power transformation. For the normality of residuals and constant error assumptions, a random distribution of residuals along the straight lines is expected as can be observed in almost all the sub-Figures a and b of the responses implying the validity of the assumptions. Using 95% confidence limits, the models' prediction accuracy were validated. Sub-figures c are the models' validation plots where in almost all the figures, the predicted values were found to be in close conformity with the experimental values. The sub-figures d represents Box-Cox for power transformation plots where it is expected that value of lambda lies within 95% confidence interval, by 95% confidence interval it means the blue lying between the reds lines with lambda value of 1 implying no need for transformation which has also been achieved in all. It is important to note the model diagnostics and validations are the final criteria used here for the checks of credibility, adequacy and accuracy of models prediction. And all the

models developed satisfied the criteria affirming the capability of the models to predict the dependent variables (factors) of concern studied here.

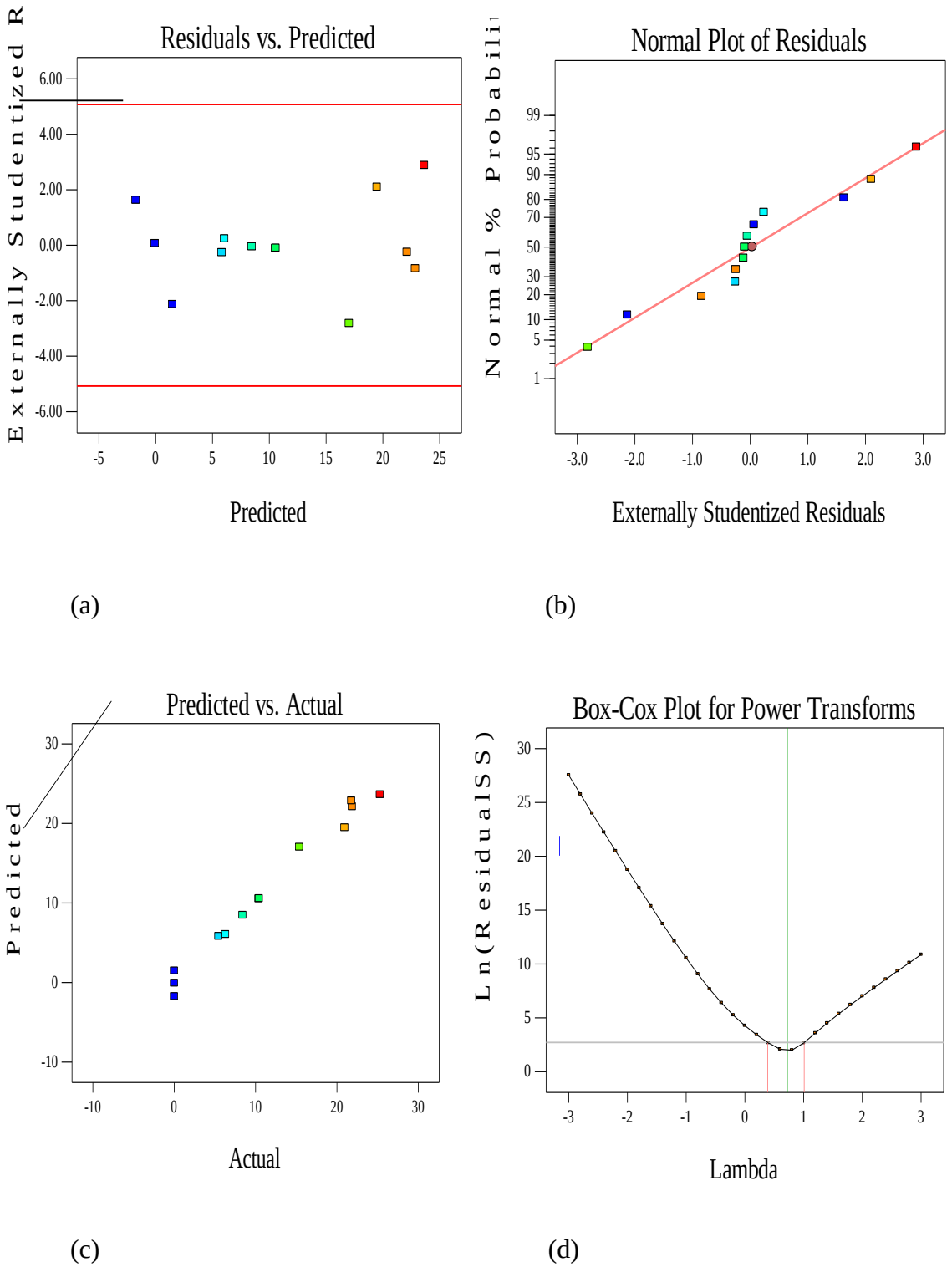


Figure 5.12: Cd removal Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

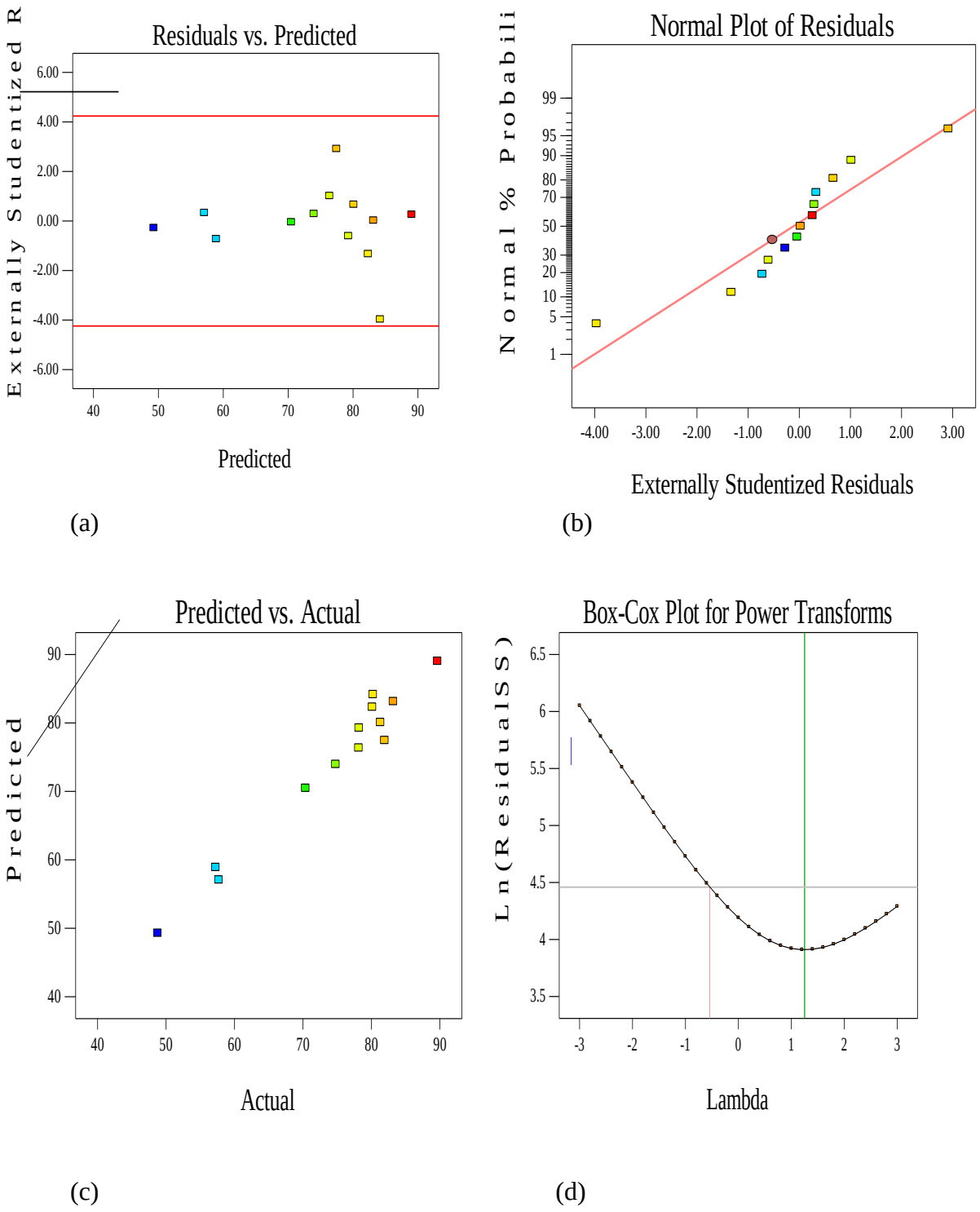


Figure 5.13: Cr removal Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation.

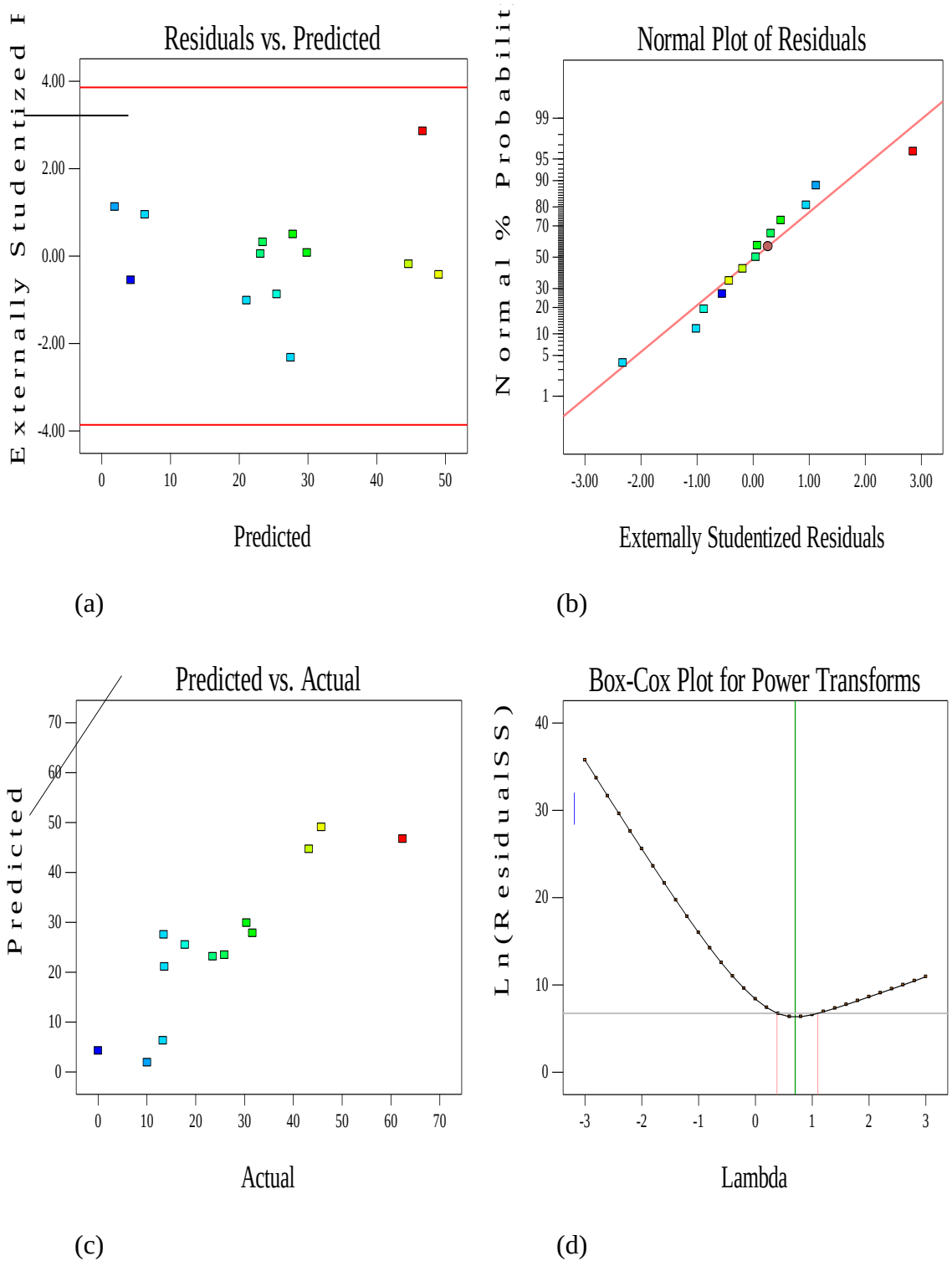
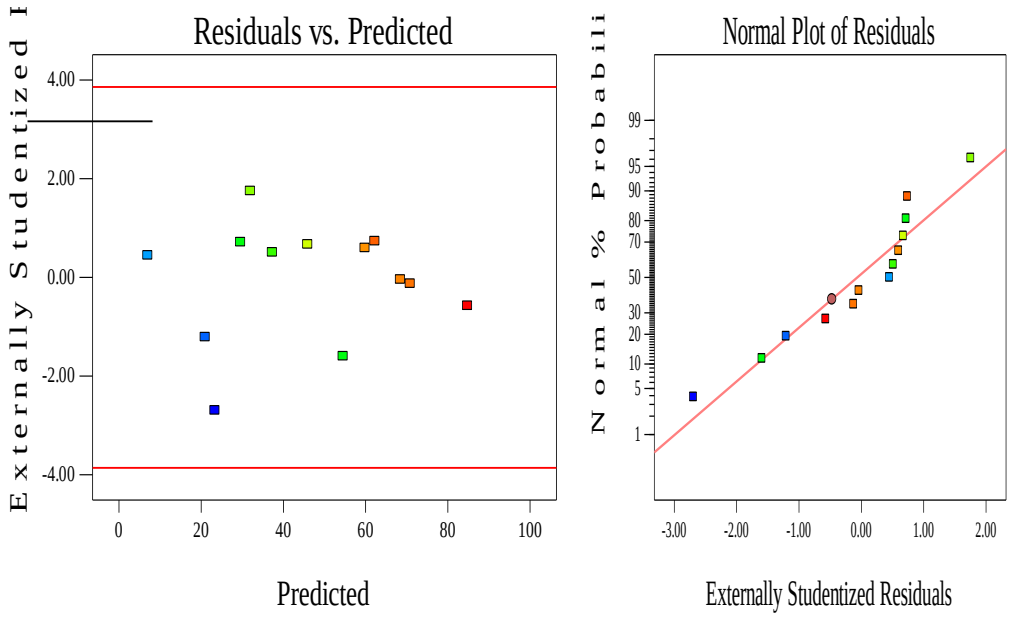
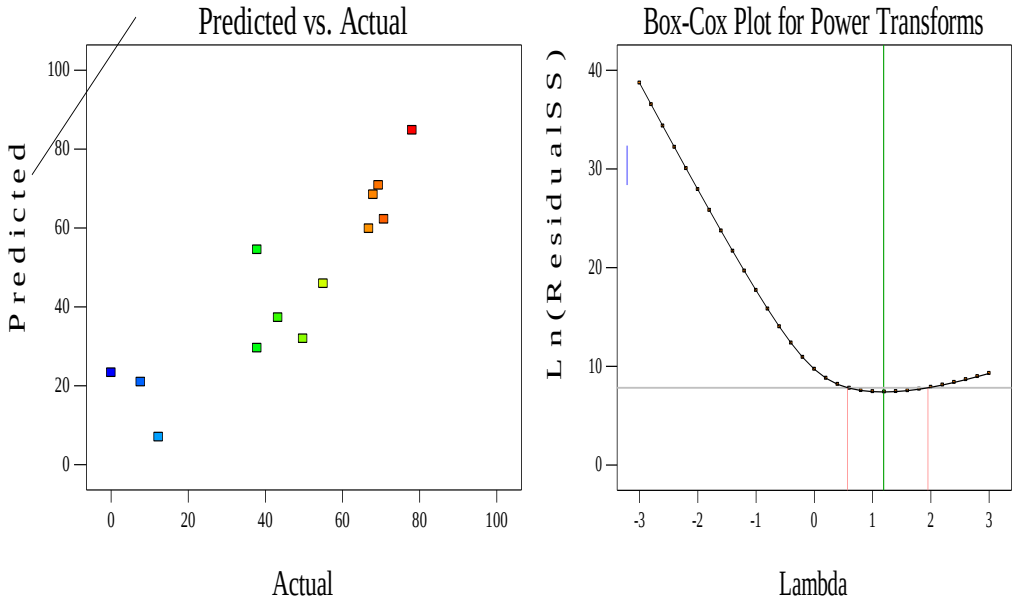


Figure 5.14: Cu removal Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation



(a) (d)



(c) (d)

Figure 5.15: Hg removal Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

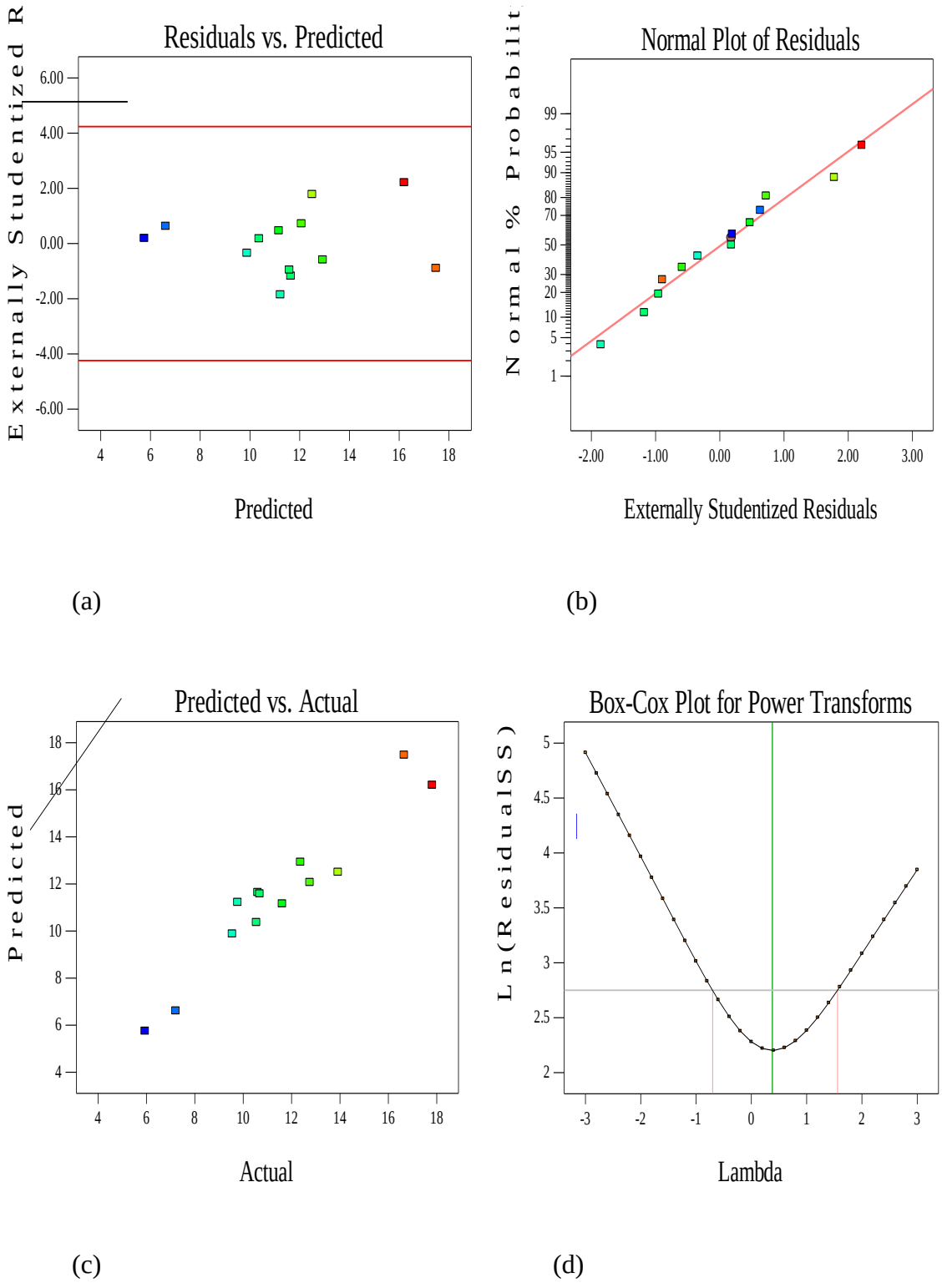


Figure 5.16: Pb removal Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

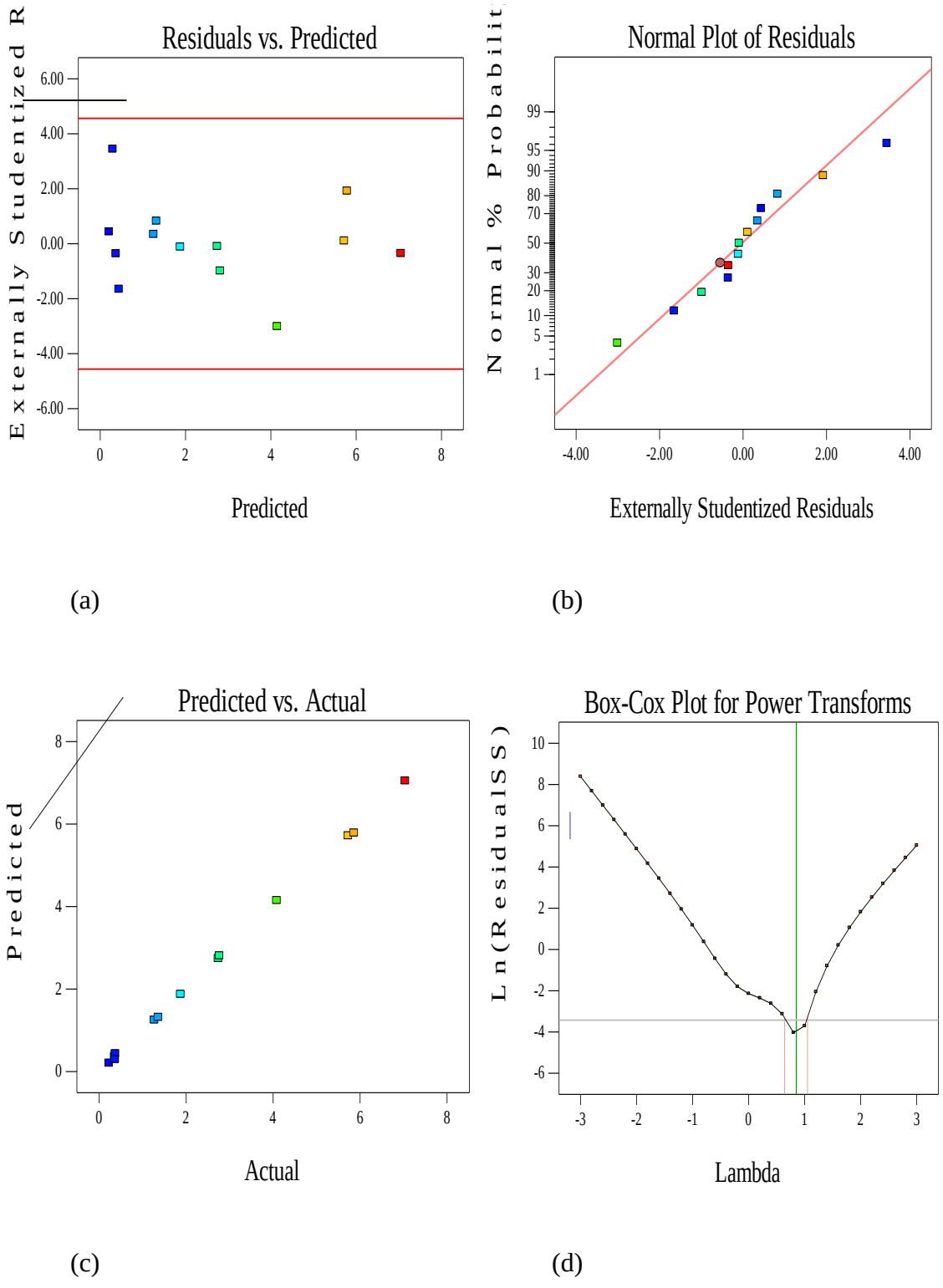


Figure 5.17: Energy consumption Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

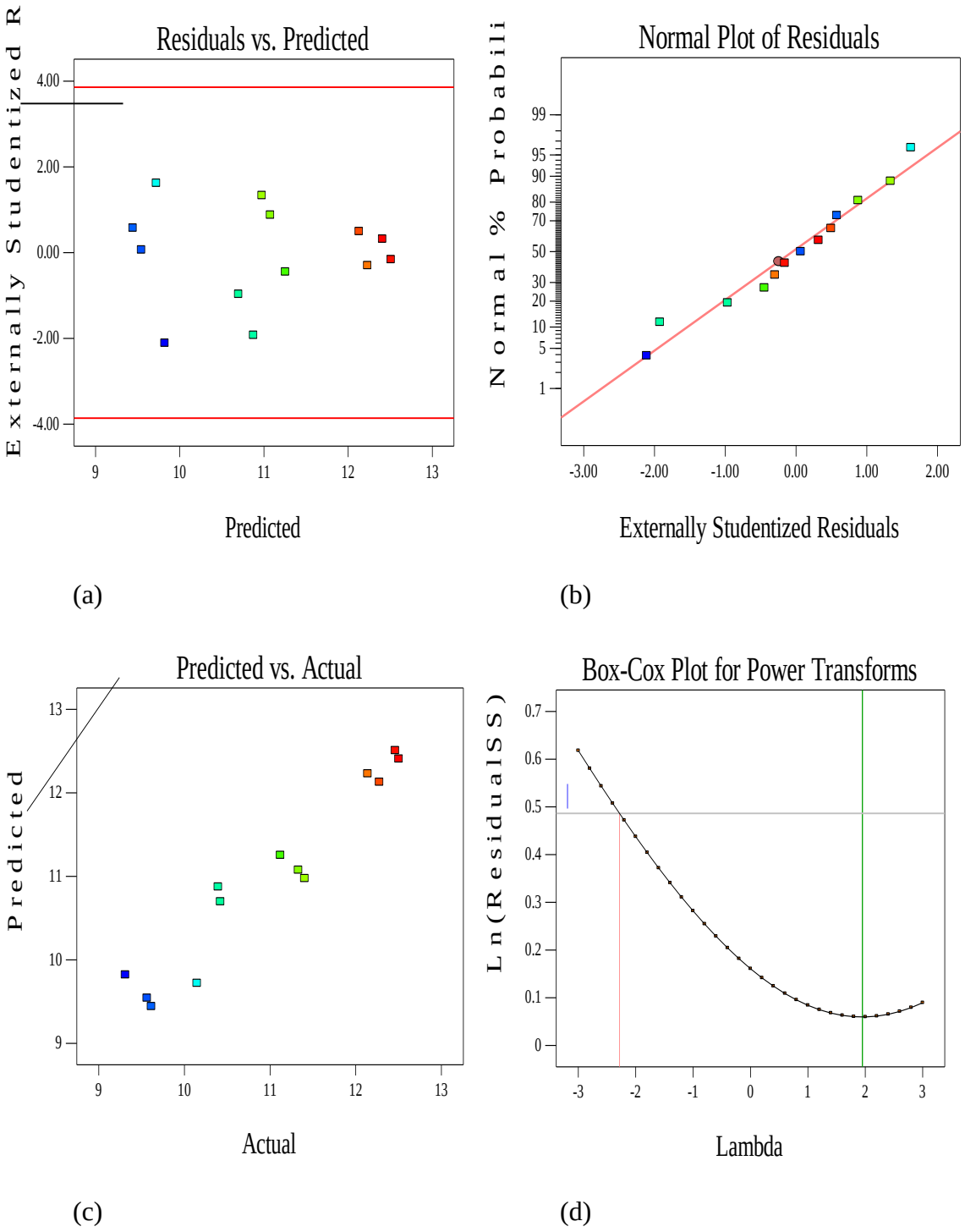


Figure 5.18: Soil pH Model Diagnostics plots for (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

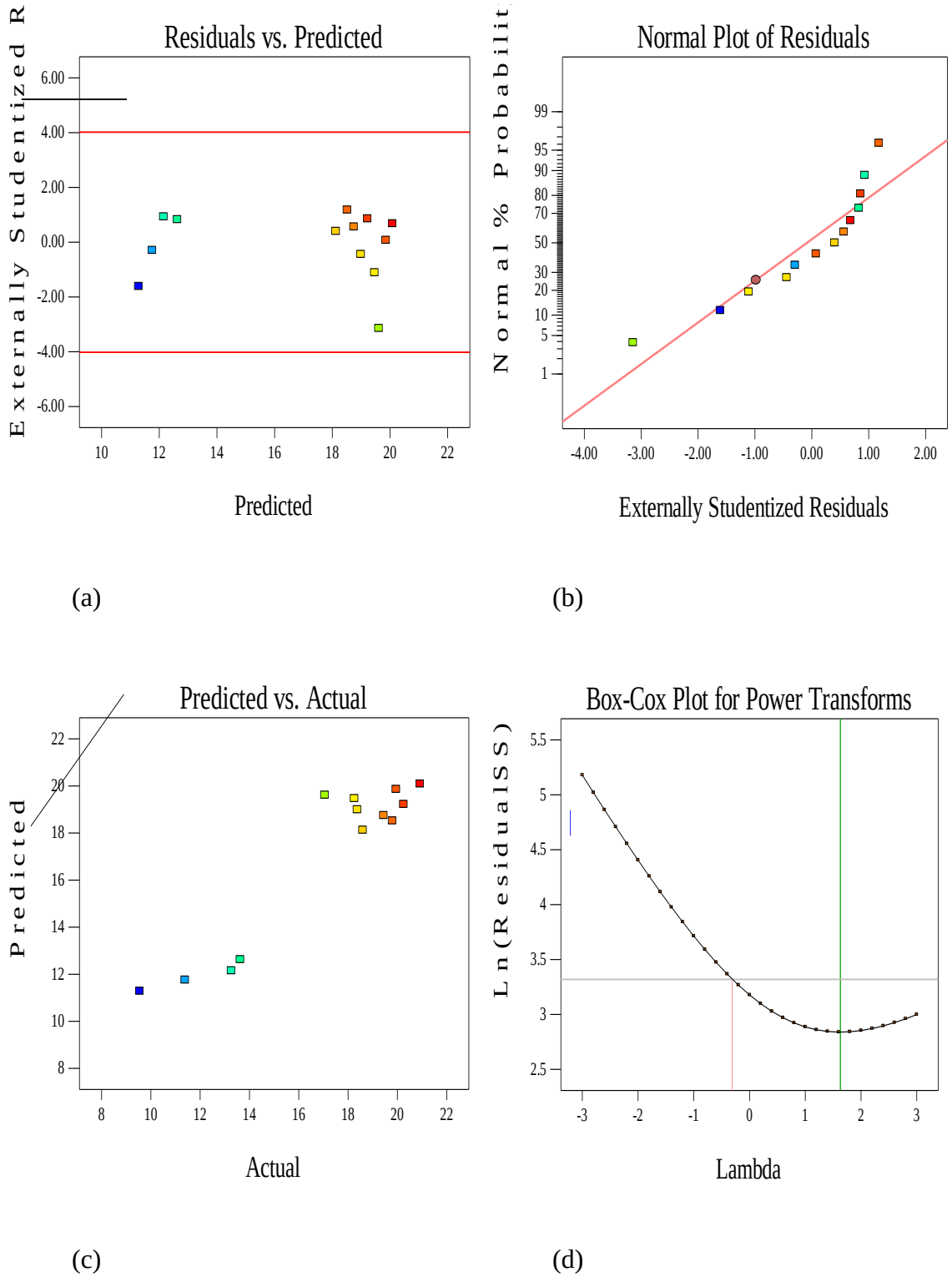


Figure 5.19: Soil Electrical Conductivity Model Diagnostics plots (a) Constant error assumption, (b) Normality assumption, (c) Model Validation: Actual vs Predicted and (d) Power transformation

5.3.4 Response Surface 3D-Plots Showing the Effect of the Factors on the Responses

In this section, 3D response surface and contour plots were developed based the response surface models generated (equations 5.8 to 5.15). The models are generated based on the experimental data and proved by all statistical test and assumptions to be valid at 95% confidence interval, giving some confidence level in relying on the information obtained from this plots. These plots help us to further observe and understand the effects of the independent variablesof concern (voltage gradient, pulse duty cycle and bentonite to clay ration) on the responses in this study ranging from heavy metals removal efficiency, energy consumption, soil pH and soil electrical conductivity.

Heavy metals removal efficiency: Figures 5.20 to 5.29 presents the 3D response surface and contour plots showing the effect of voltage gradient, pulse duty cycle and bentonite ratio on the heavy metals removal efficiencies based on the 13 experimental results over 3 weeks of treatment time. It can be clearly observed from the figures that increase in voltage gradient from 0.2 to 0.6 increases the removal efficiency which may be due to increase in mobility of the heavy metals ions as a result of increase in potential difference. However, in some heavy metals like cadmium and copper, increase in voltage gradient decreases the removal efficiency, this may be due to high current generated leading to high electroosmotic flow towards cathode which opposes the anionic species moving towards anode [40]. The removal efficiency in all the heavy metals have been shown to decrease with increase in bentonite ratio, the decrease may due to higher surface area possessed by the bentonite of 42.13m^2/gas compared to the clay with 9.07m^2/g which will increase the tendency of heavy metals adsorption onto the surface

and ultimately reduce the removal efficiency electrokinectic. Other possible factors that may lead to decrease in removal efficiency are precipitation and ion exchange [11, 81]. It can also be observed from the figures that in all cases of heavy metals , increase in pulse duty cycle from 0.5 to 0.9 increases the removal efficiencies which may be due to increase in overall treatment time. It worth knowing that higher pulse duty cycle means higher current flow time.

Energy consumption: Figures 5.30 and 5.31 depicts the variation of the three (3) factors with energy consumption, It can be clearly observed from the curvature of figure 5.30 how increase in voltage gradient from 0.2 to 0.6 increases the energy, this is due to the fact that increase in voltage gradient increases both voltage and current and energy consumed which is the product of the two will ultimately rise. The increase in bentonite ratio leads to increase in energy consumption which can hardly be observed from the 3D plot but is evident from equation 5.13.It can also be observed from figure 5.31 that increase in pulse duty cycle leads to increase in energy consumption which is due increase in overall run time leading more current usage and ultimately more energy consumption.

Soil pH and Electrical conductivity: Figures 5.32 to 5.35 shows the variation of soil pH and electrical conductivity with the factors and has shown clearly that increase in voltage gradient increases both the two significantly but less effect of pulse duty cycle and bentonite ratio be noticed. It is very important to realize that all the observations here is a corroboration of the observations made in earlier part of this chapter. The 3D plots here give a complete visualization of

the relationship between the independent variable and the depended in a clearer and more convincing picture.

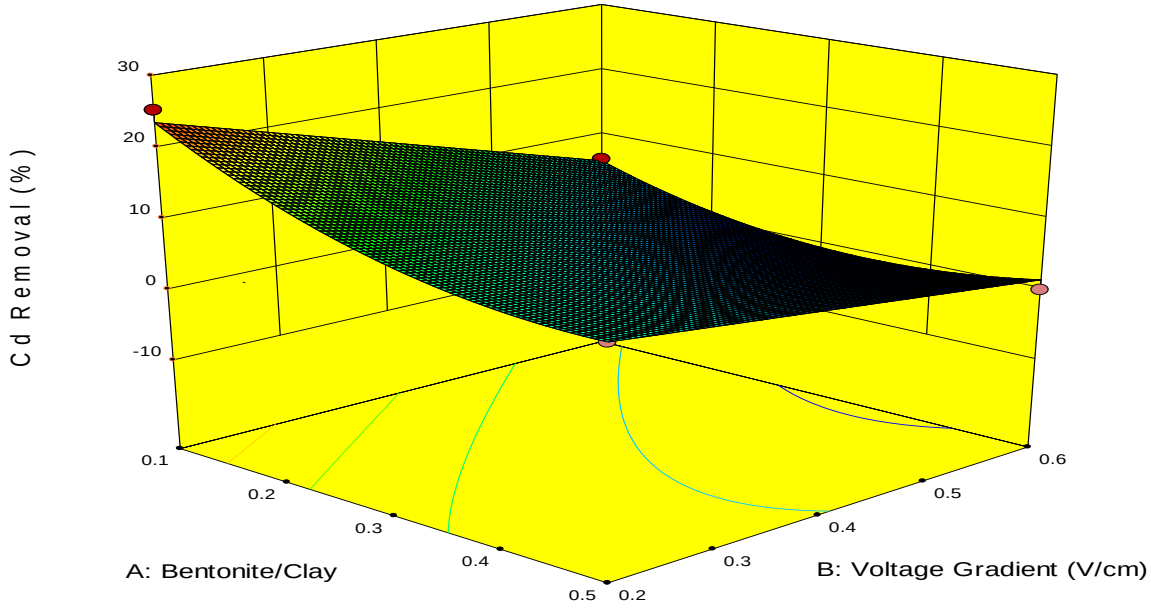


Figure 5.20: Effects of Bentonite/clay and Voltage gradient on Cd Removal

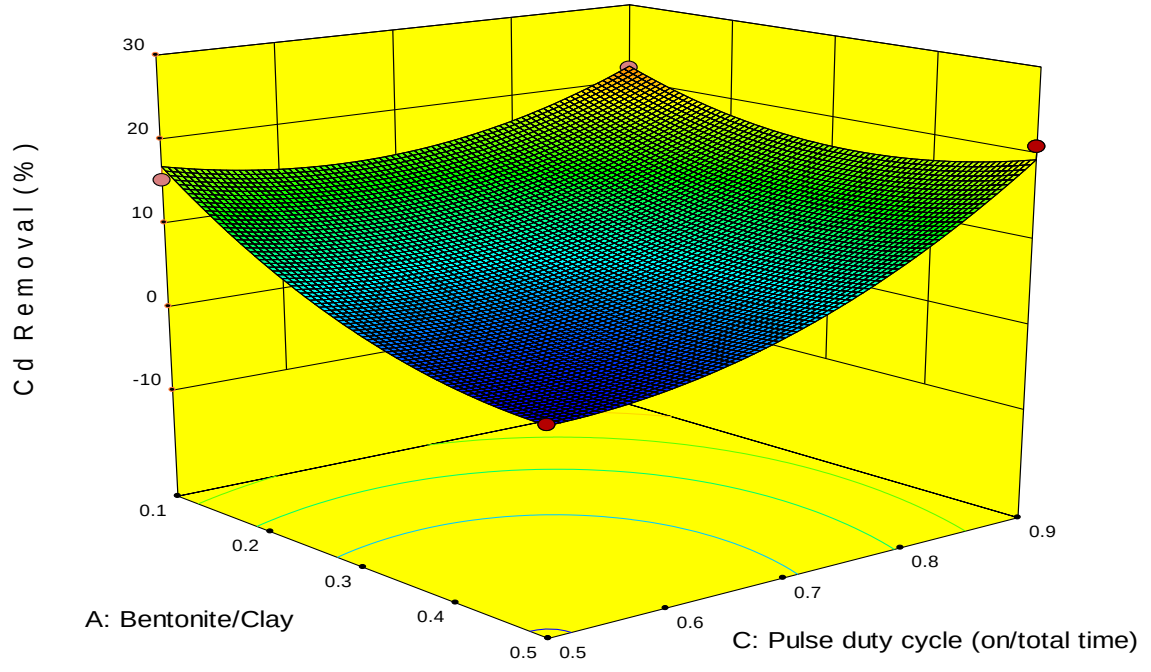


Figure 5.21: Effects of Bentonite/clay and Pulse duty cycle on Cd Removal

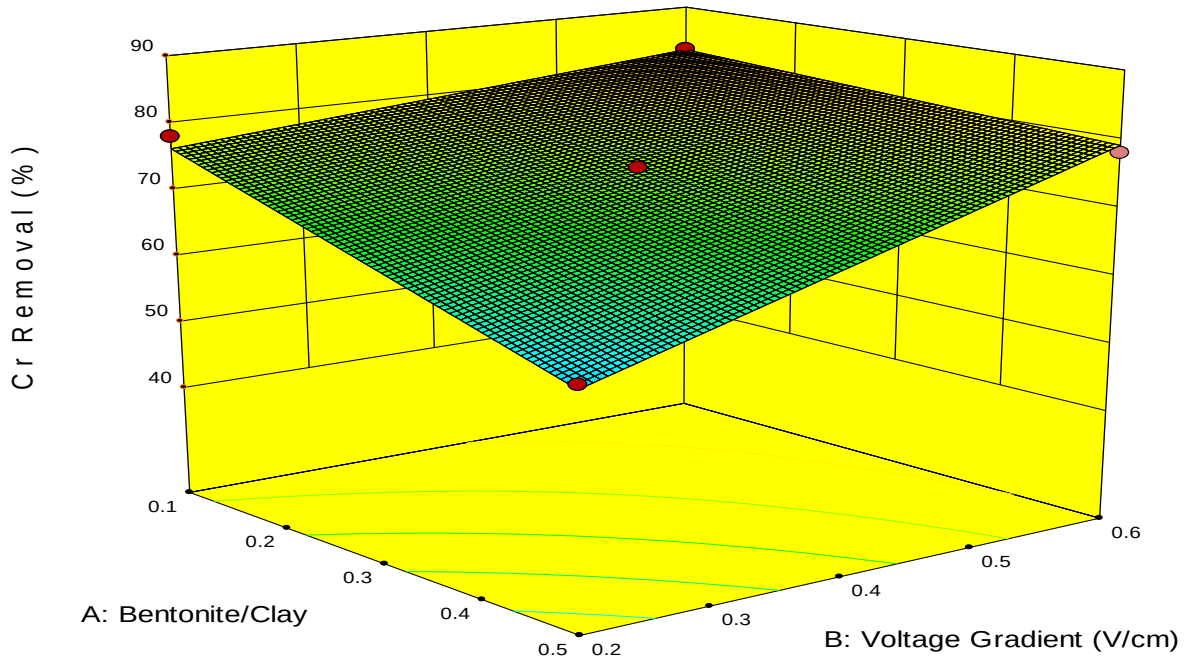


Figure 5.22: Effects of Bentonite/clay and Voltage gradient on Cr Removal

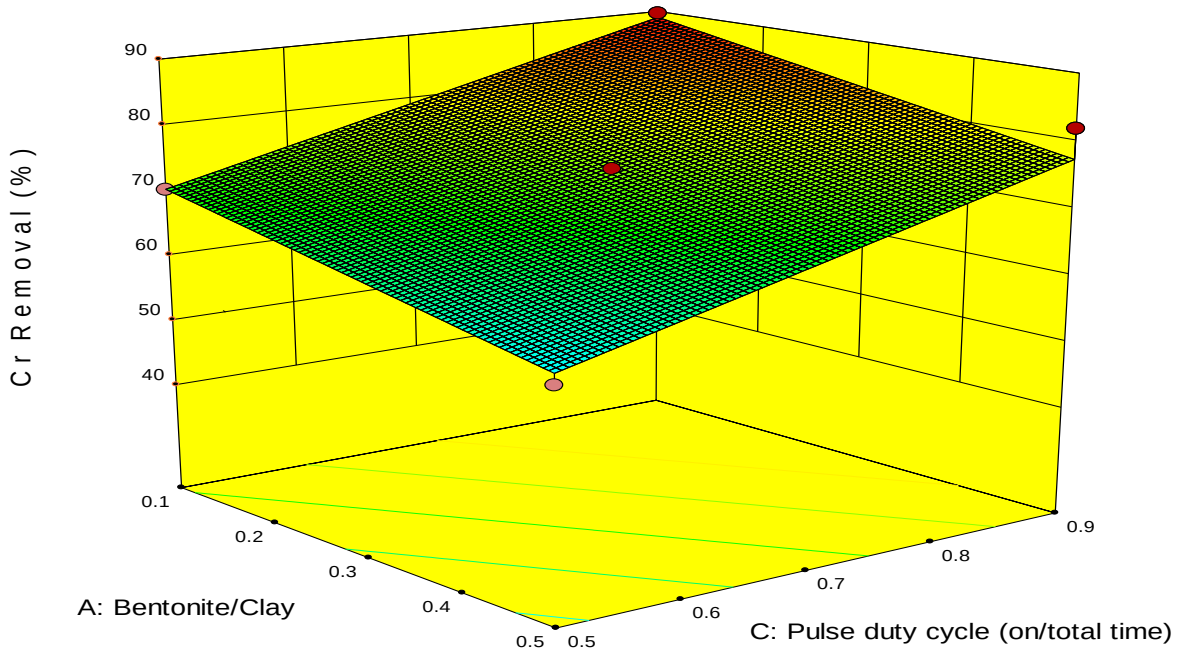


Figure 5.23: Effects of Bentonite/clay and Pulse duty cycle on Cr Removal

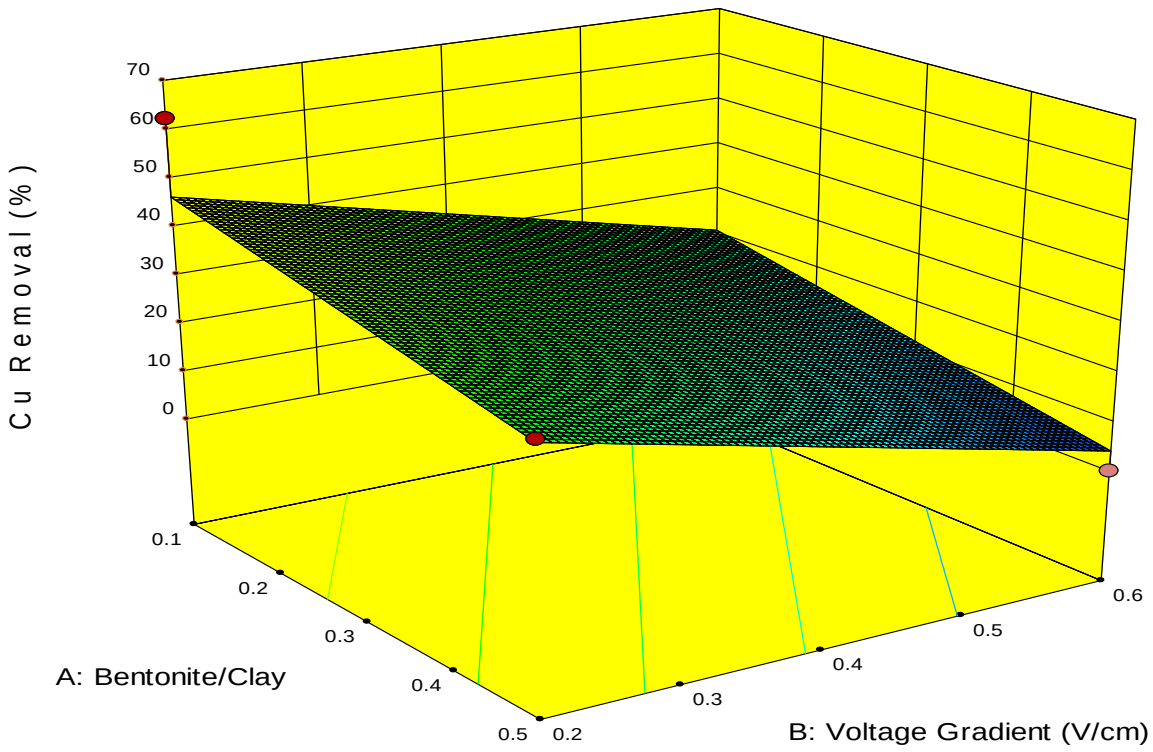


Figure 5.24: Effects of Bentonite/clay and Voltage gradient on Cu Removal

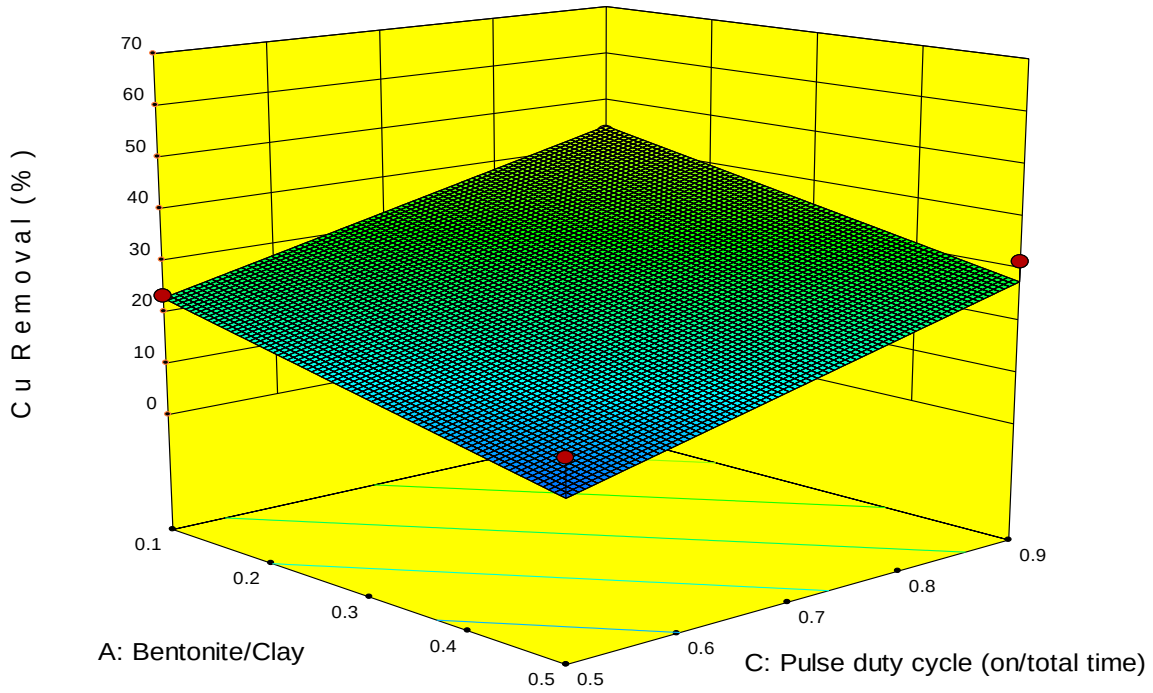


Figure 5.25: Effects of Bentonite/clay and Pulse duty cycle on Cu Removal

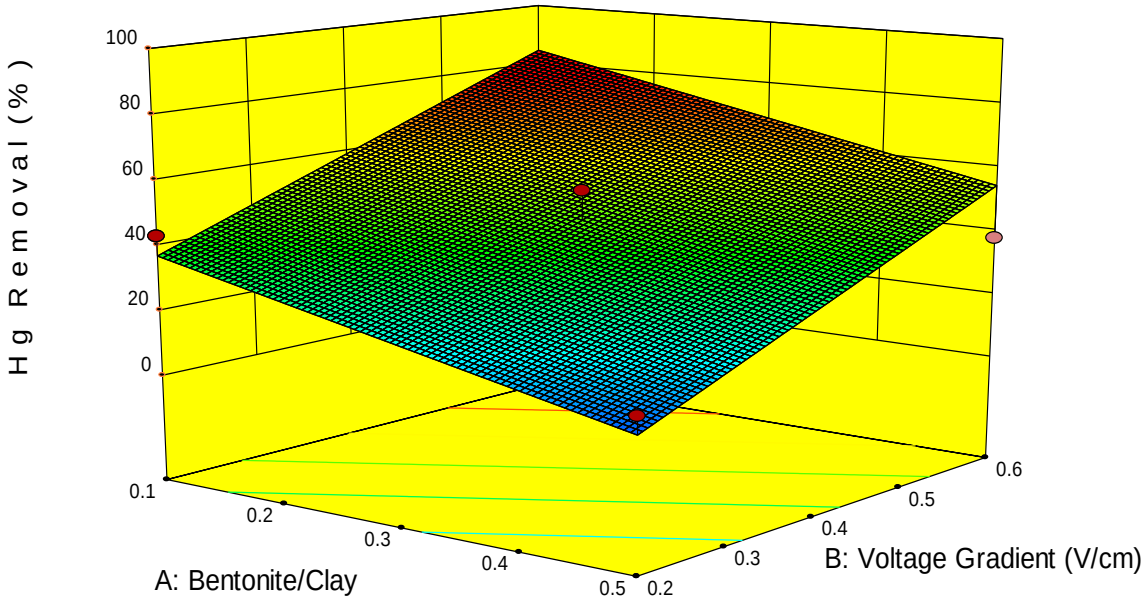


Figure 5.26: Effects of Bentonite/clay and Voltage gradient on Hg Removal

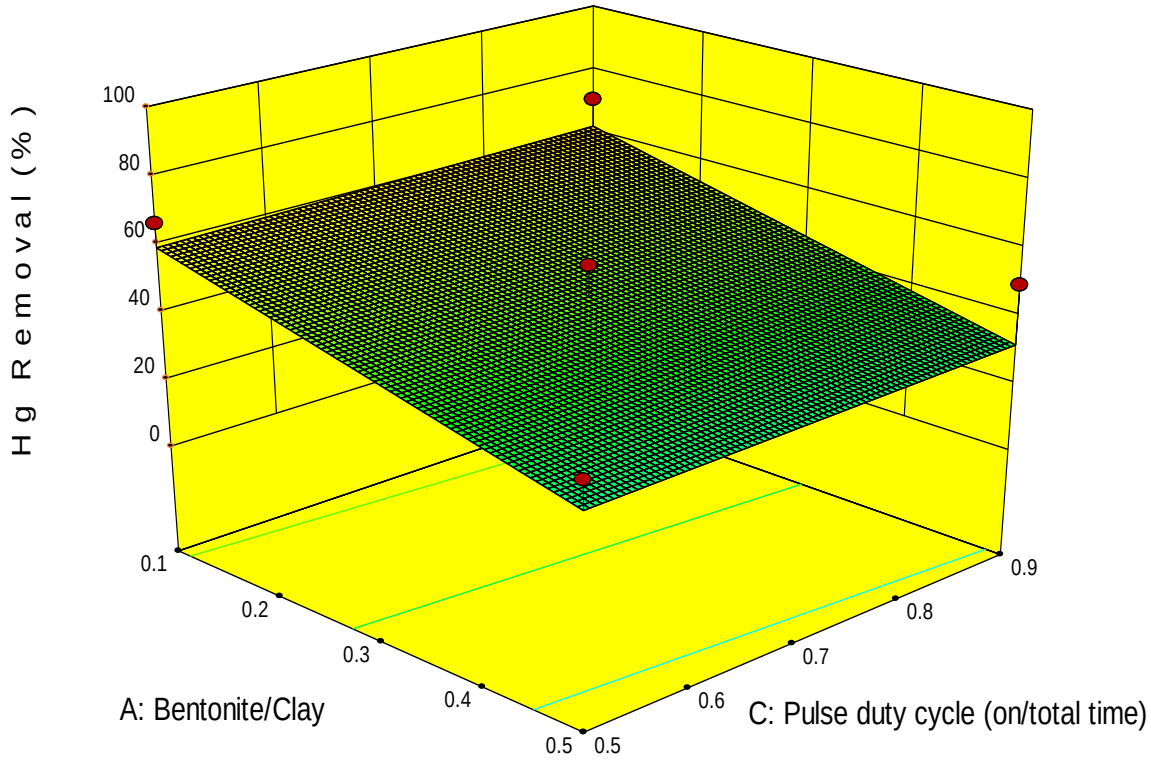


Figure 5.27: Effects of Bentonite/clay and Pulse duty cycle on Hg Removal

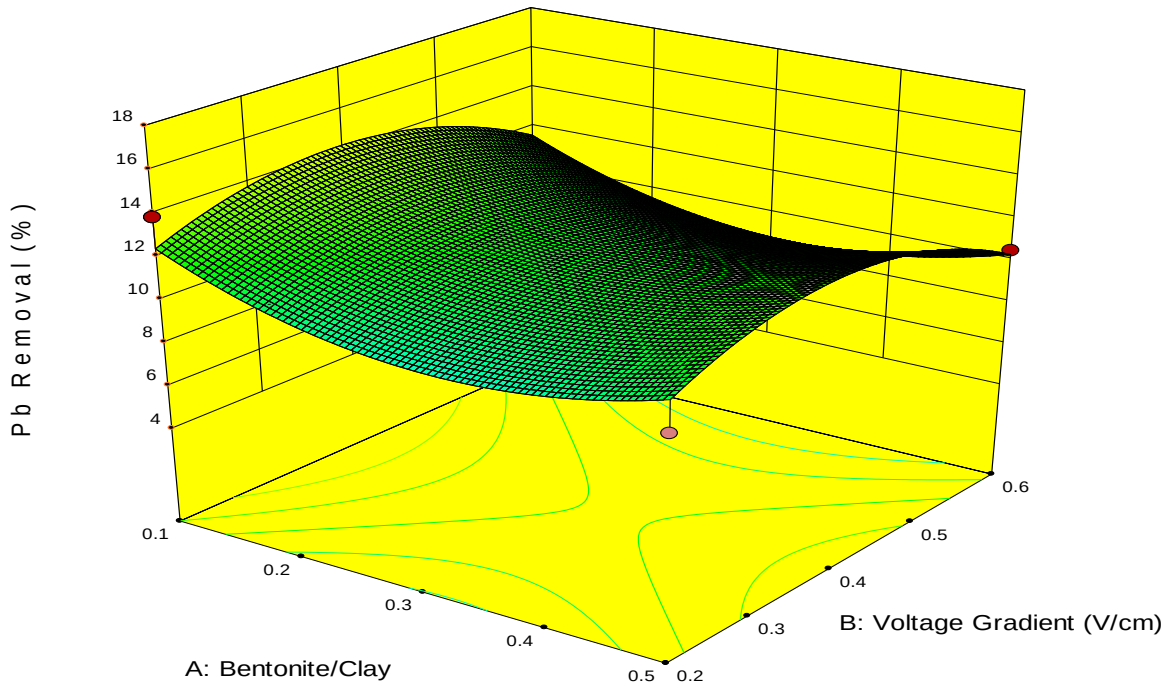


Figure 5.28: Effects of Bentonite/clay and Voltage gradient on Pb Removal

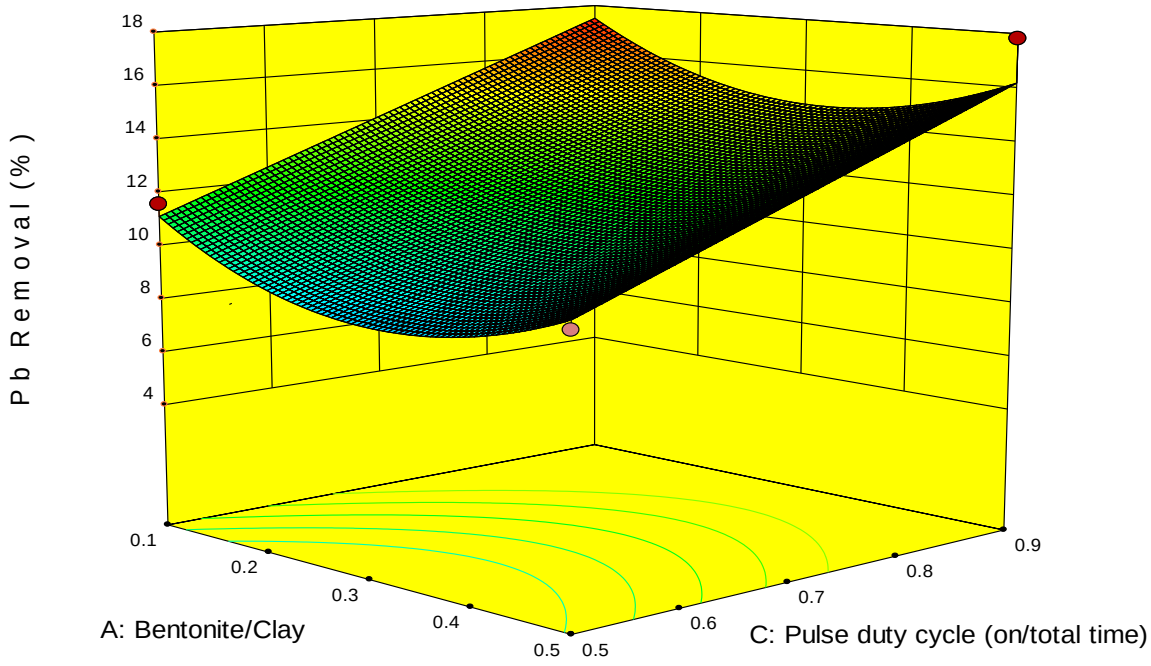


Figure 5.29: Effects of Bentonite/clay and pulse duty cycle on Pb Removal

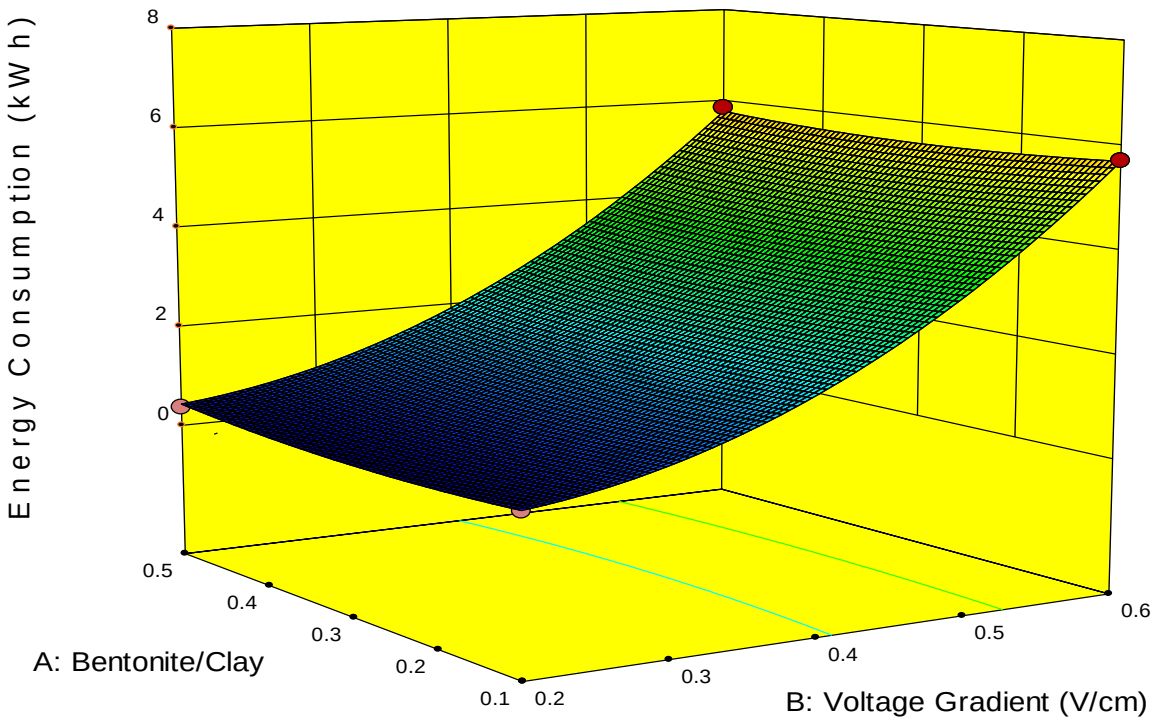


Figure 5.30: Effects of Bentonite/clay and Voltage gradient on Energy Consumption

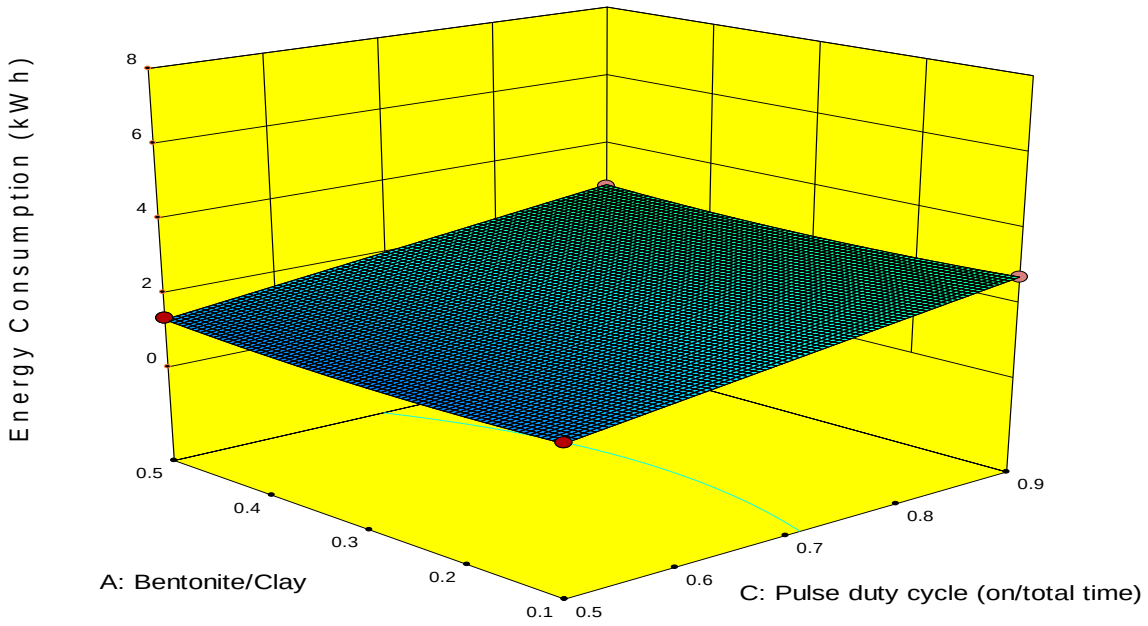


Figure 5.31: Effects of Bentonite/clay and Pulse duty cycle on Energy consumption

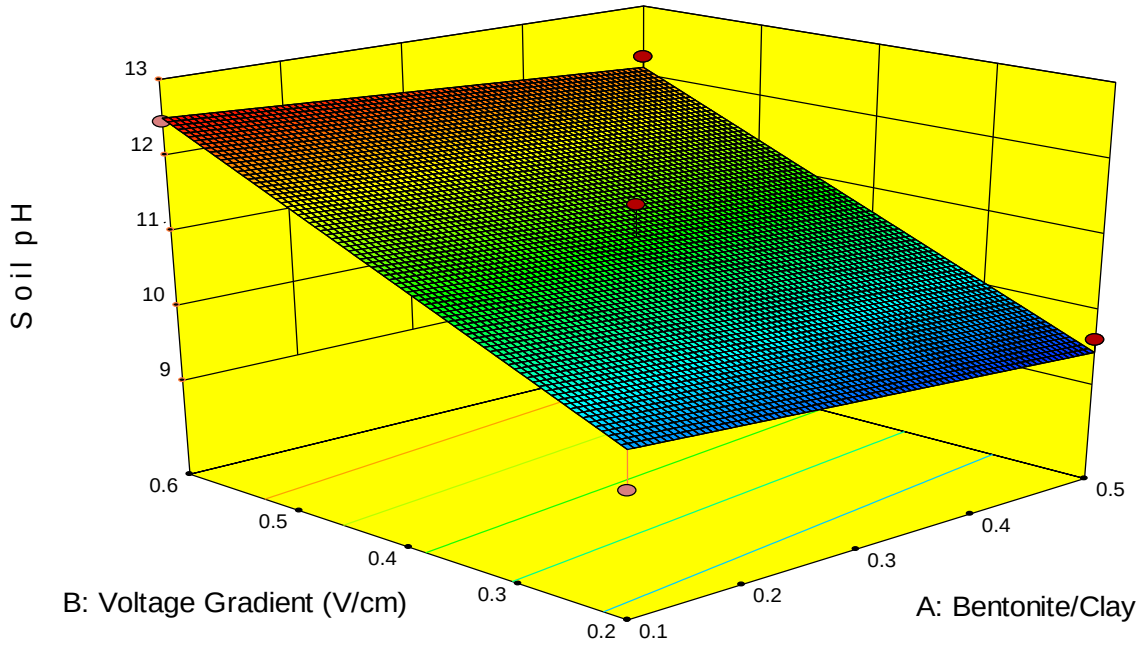


Figure 5.32: Effects of Bentonite/clay and Voltage gradient on Soil pH

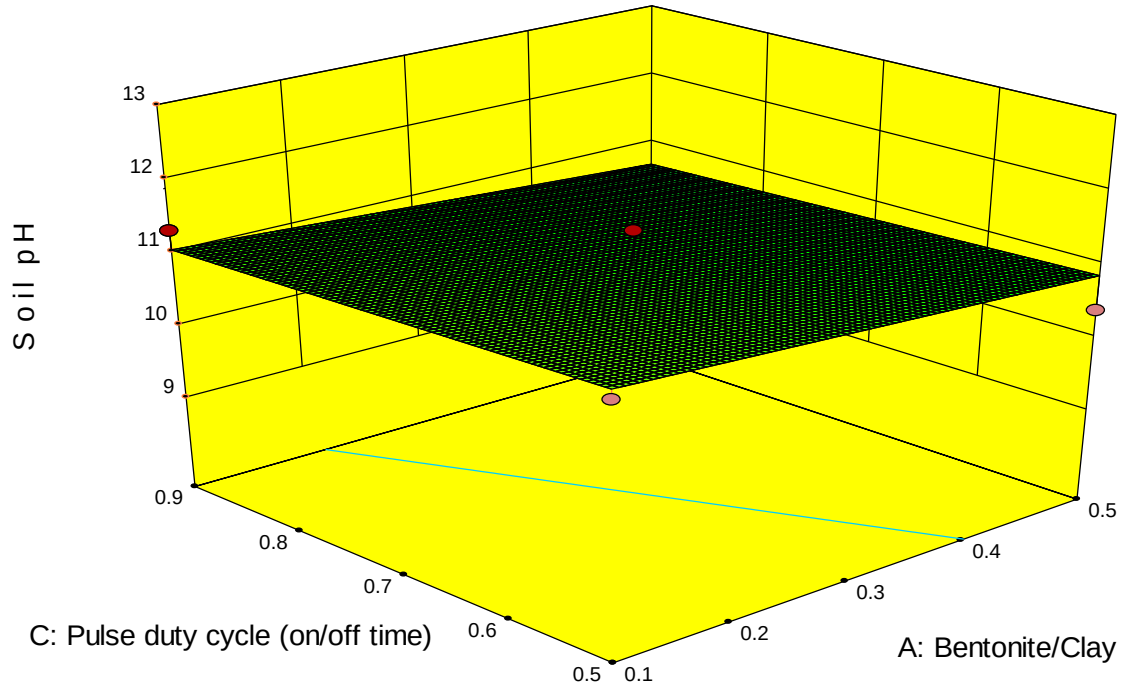


Figure 5.33: Effects of Bentonite/clay and Pulse duty cycle on Soil pH

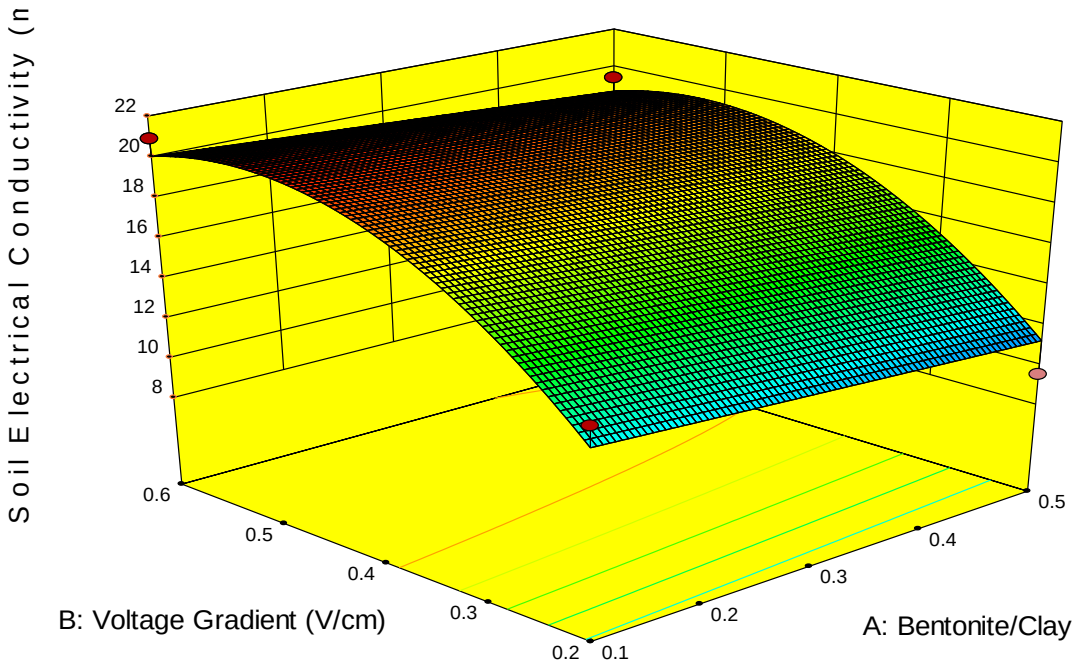


Figure 5.34: Effects of Bentonite/clay and Voltage gradient on Soil Electrical Conductivity

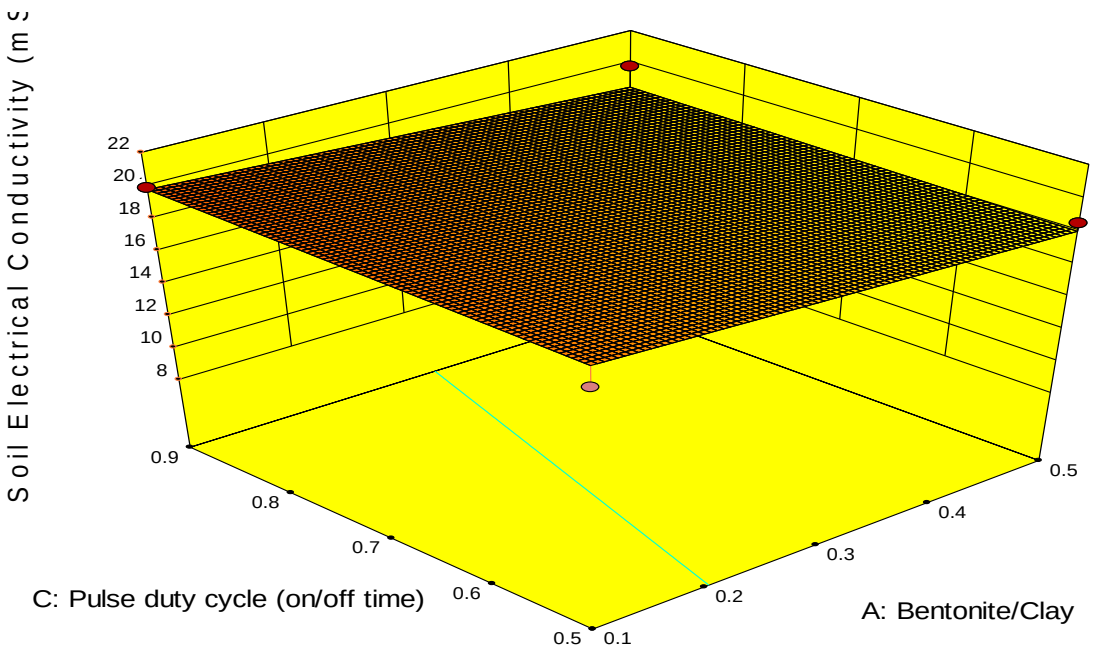


Figure 5.35: Effects of Bentonite/clay and Pulse duty cycle on Soil Electrical Conductivity

5.3.5 Perturbation Plots and Sequence of Influential Factors:

Perturbation plots give the nature of factor effect whether protagonistic or antagonistic to the response and the sequence of factors according to degree of influence. A steep slope signifies sensitivity of a factor to the response and as the line tends towards a flat line signifies low sensitivity when the model is in any form of quadratic natureas in figures 5.36, 5.40, 5.41 and 5.43 respectively for Cd removal, Pb removal, energy consumption and soil electrical conductivity. If on the other hand the model is a linear or two factor interaction, only the nature of the factor effect will be obtained from the perturbation plot but the sensitivity wise will be derived from model equation alone [117], as in figures 5.37, 5.38, 5.39 and 5.42 for Cr removal, Cu removal, Hg removal and Soil pH Models respectively. The contribution and relative effect of individual factor and its interaction in a given model is function of its coefficient. From the perturbation plots depicted in figures 5.36 to 5.43 and the model equations 5.8 to 5.15. A sequence of factors is develop according to the degree of influence and the nature of the effect being either positive or negative which was also obtained from both the 3D response surface and the sign of the coefficient of a factor in the model equation. The sequence of the influential factors and the nature of their effect are shown in the Table 5.14.

Table 5.13: Sequence of influential factors and nature of their effect

Response	Sequence of factor influence and nature of effect
Cd removal, %	C (Positive) > B (Negative) > A (Negative)
Cr removal, %	C (Positive) > B (Positive) > A (Negative)
Cu removal, %	B (Negative) > C (Positive) > A (Negative)
Hg removal, %	B (Positive) > A (Negative) > C (Positive)
Pb removal, %	C (Positive) > A (Positive) > B (Negative)
Energy Consumption, $Kwhr/m^3$	B (Positive) > C (Positive) > A (Positive)
Soil Electrical Conductivity, mS/cm	B (Positive) > A (Negative) > C (Positive)
Soil pH	B (Positive) > A (Negative) > C (Negative)

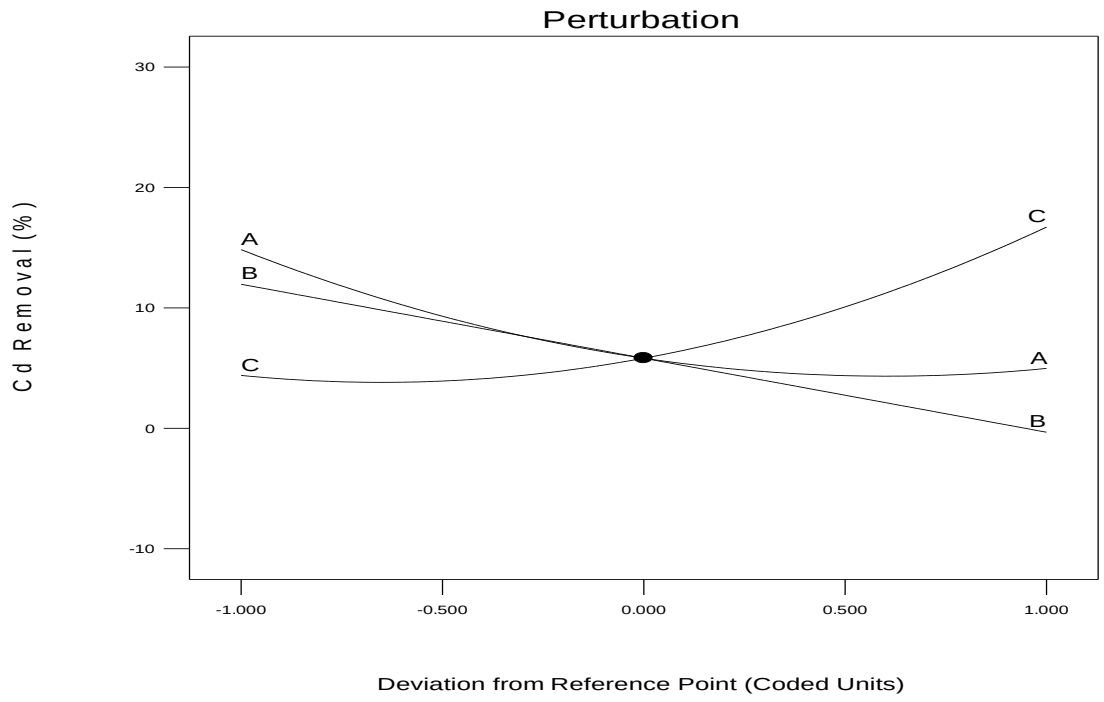


Figure 5.36: Perturbation plots showing the degree of influence of factors on Cd removal

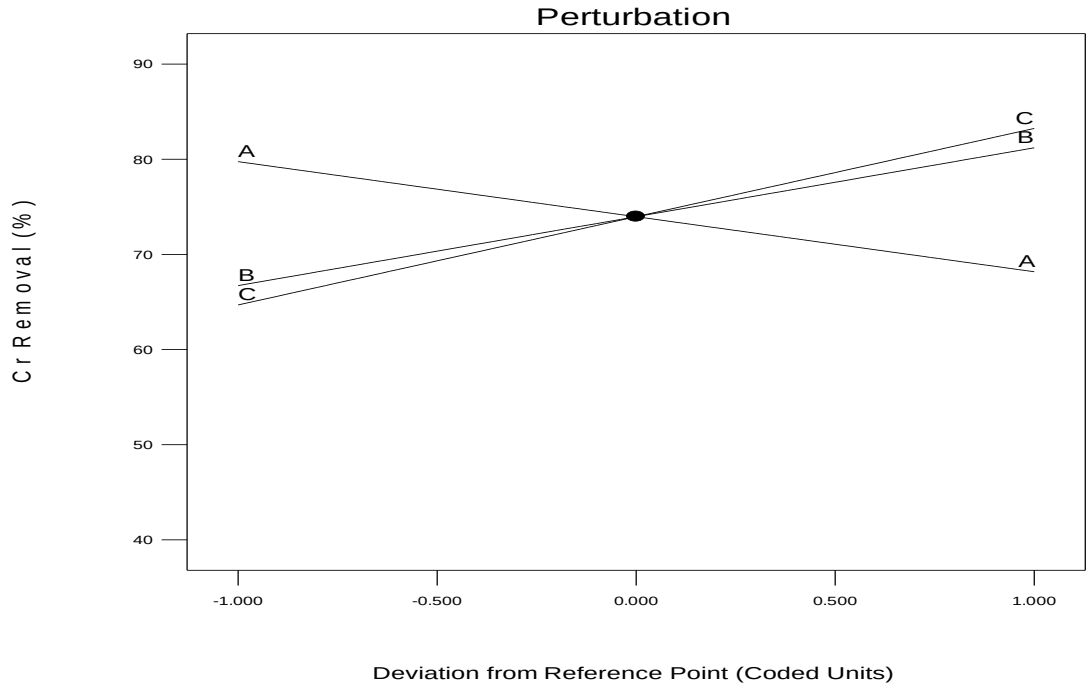


Figure 5.37: Perturbation plots showing the degree of influence of factors on Cr removal.

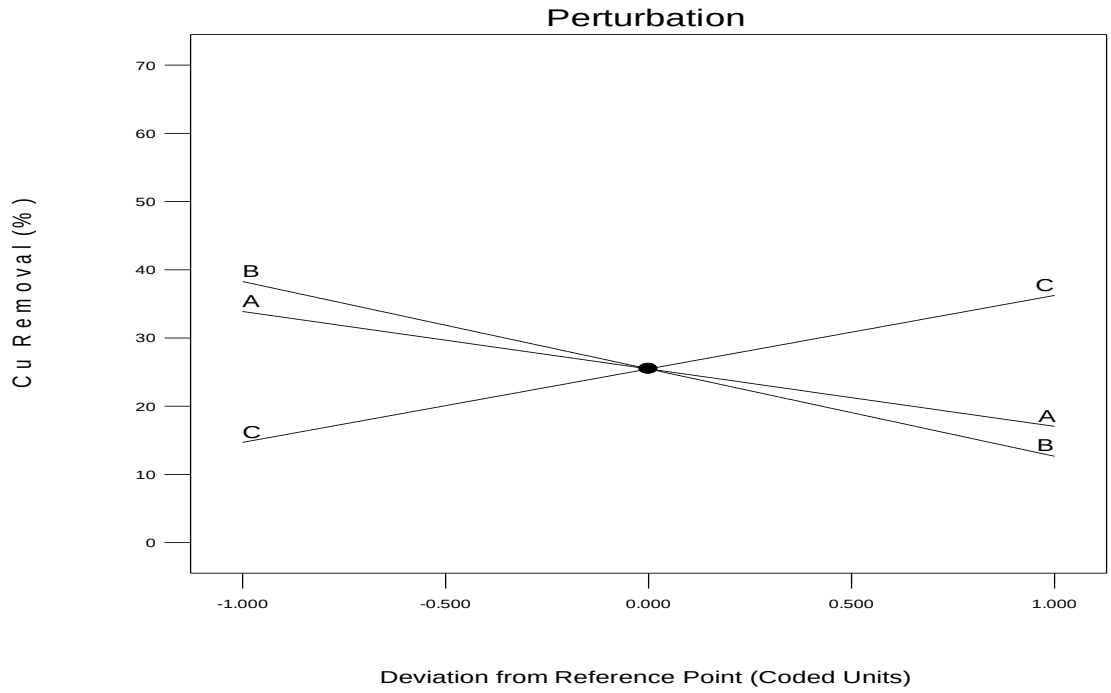


Figure 5.38: Perturbation plots showing the degree of influence of factors on Cu removal

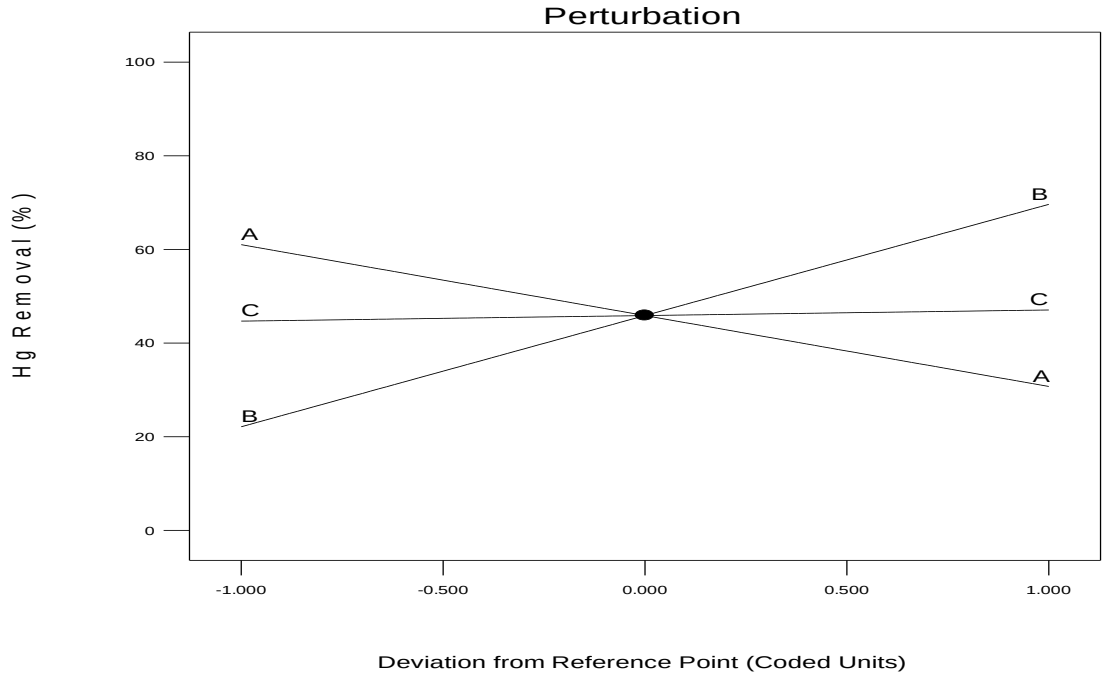


Figure 5.39: Perturbation plots showing the degree of influence of factors on Hg removal

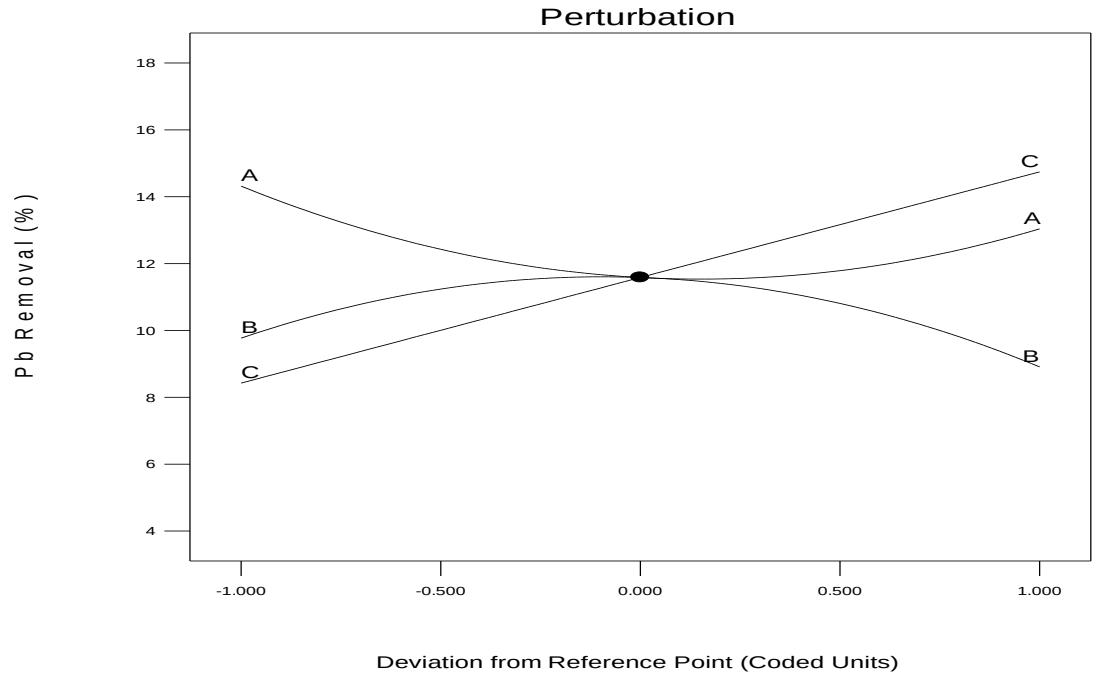


Figure 5.40: Perturbation plots showing the degree of influence of factors on Pb removal

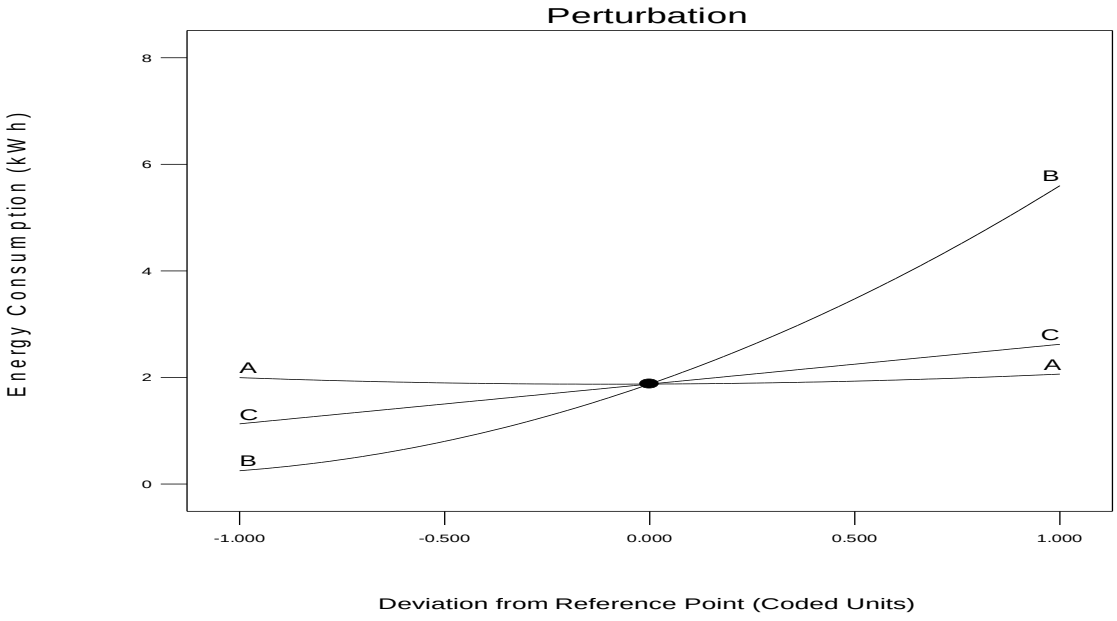


Figure 5.41: Perturbation plots showing the degree of influence of factors on Energy consumption

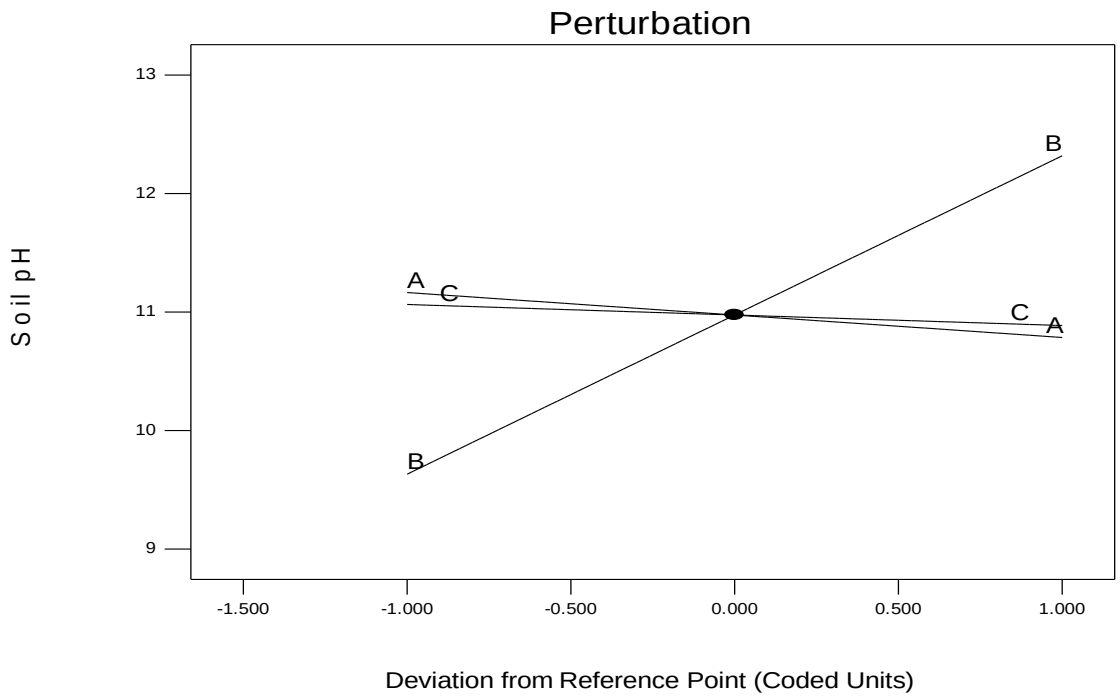


Figure 5.42: Perturbation plots showing the degree of influence of factors on Soil pH

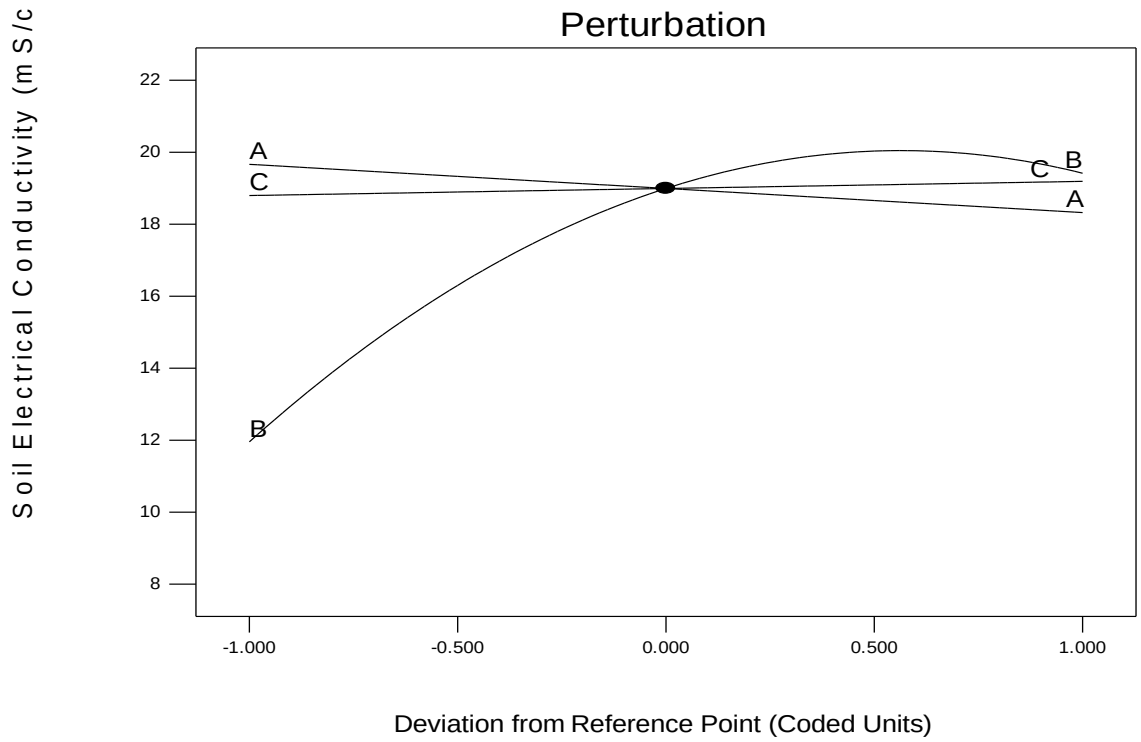


Figure 5.43: Perturbation plots showing the degree of influence of factors on soil electrical conductivity

5.3.6 Optimization of Heavy Metals Removal Efficiencies and Energy Consumption

The process was optimize with a target of maximizing heavy metals removal efficiencies and minimizing energy consumption with the help of numerical optimization tool in the Design Expert software which uses its algorithm to search in the design space the best factor settings that meet the desired goals. The optimization was simultaneously done based on the developed models. During this, the goals were set and hence the optimization which generates 20 solutions of which the best was selected as presented in Table 5.15 below. The table reveals the combine optimal conditions for maximizing simultaneous removal efficiencies of the heavy metals and minimizing energy consumption with a good overall desirability value of 0.86 which is closer to one implying high probability of meeting the set goals [117]. Desirability function gives a value ranging from zero (0) to one (1) with 0 signifying difficulty in achieving the target goals set and 1 implying easiness in achieving the set goals. However, an overall desirability gives an overall value for achieving optimization goals for multiple responses simultaneously [132].

Table 5.14: Optimization results for contaminants removal efficiencies and Energy consumption

Constraints				Optimization results
Name	Goal	Lower limit	Upper limit	Overall desirability(0.86)
A: Bentonite/Clay	Is in range	0.1	0.5	0.10
B: V. G (V/cm)	Minimize	0.2	0.6	0.24
C: P.D.C (on/total time)	Is in range	0.5	0.9	0.90
Cd Removal (%)	Maximize	0	25.3	27.16
Cr Removal (%)	Maximize	48.77	89.64	92.78
Cu Removal (%)	Maximize	0	62.41	54.71
Hg Removal (%)	Maximize	0	78.06	43.58
Pb Removal (%)	Maximize	5.94	17.81	16.43
Energy Consumption(kwh)	Minimize	0.223	7.04	0.74

Table 5.15: RSM Optimization Numerical Solutions

N/S	B/C	V.G	PDC	Cd	Cr	Cu	Hg	Pb	E.C	Desirability
1	0.10	0.24	0.90	27.17	92.78	54.71	43.58	16.43	307.08	0.863
2	0.10	0.25	0.90	27.10	92.73	54.57	43.84	16.46	315.00	0.863
3	0.10	0.24	0.90	27.09	92.59	54.57	43.58	16.40	306.67	0.862
4	0.10	0.25	0.90	26.89	92.56	54.13	44.66	16.57	340.83	0.862
5	0.10	0.24	0.90	26.99	92.36	54.41	43.59	16.35	306.25	0.861
6	0.10	0.25	0.90	26.83	92.51	54.00	44.89	16.60	348.33	0.861
7	0.10	0.25	0.90	26.86	92.28	54.13	44.13	16.43	322.92	0.861
8	0.10	0.24	0.90	27.07	92.59	54.55	43.19	16.32	302.92	0.861
9	0.10	0.26	0.90	26.71	92.42	53.76	45.35	16.65	363.75	0.860
10	0.10	0.25	0.89	26.83	92.14	54.09	43.99	16.38	317.92	0.860
11	0.10	0.25	0.90	26.77	92.22	53.93	44.53	16.48	335.42	0.860
12	0.10	0.24	0.89	26.83	91.95	54.11	43.59	16.28	305.42	0.860
13	0.10	0.24	0.89	26.75	91.76	53.97	43.60	16.24	305.00	0.859
14	0.10	0.27	0.90	26.50	92.26	53.33	46.13	16.74	390.00	0.859
15	0.11	0.24	0.90	27.03	92.45	54.50	42.64	16.19	293.75	0.859
16	0.10	0.26	0.89	26.46	91.72	53.34	45.09	16.47	351.67	0.858
17	0.11	0.24	0.90	26.98	92.38	54.42	42.54	16.15	293.33	0.858
18	0.10	0.24	0.88	26.57	91.33	53.66	43.61	16.16	303.75	0.857
19	0.10	0.24	0.88	26.43	90.99	53.41	43.62	16.10	303.33	0.856
20	0.10	0.25	0.88	26.35	90.79	53.26	43.62	16.06	302.50	0.855

Summarily, the variation of the three factors; voltage gradient, pulse duty cycle and bentonite ratio were successfully studied, the generated models for the heavy metals removal efficiencies and energy consumption are of the form of linear, 2 factor interaction, and reduced quadratic which were generated through rigorous statistical procedure with the help of design expert software and evaluated using the different statistical and probability assumptions and tests including; P-value for model's significance, R^2, adjusted R^2, predicted R^2 and adequate Precision for model's correlation coefficient and model diagnostics and were all successful as have seen from the tables and figures. The 3D plots, equations and perturbation plots explains how each factor affects the heavy metals removal efficiencies, energy consumption, soil pH and soil electrical conductivity where in all cases Bentonite ratio increase have be seen to reduce removal efficiency and that has been attributed to its higher surface area of 42.13m^2/mg over the clay with 9.07m^2/mg, voltage gradient increase has also been noticed to increase the removal efficiencies in most cases due increase in potential difference resulting higher mobility of ions towards the opposite electrode with few cases like in Cr(IV) due to its existence as anion moving towards anode and as such will be probably be retarded due to electroosmotic flow towards the cathode. Finally was the increase in pulse duty cycle which has shown to increase the removal efficiencies but increase the energy consumption as oppose to reduction of energy consumption as anticipated, this has been realized due to pulsing in hours in this study. However, other studies that have succeeded in reducing energy consumption by pulsing as a result of pulsing in seconds and milliseconds [26, 104]. Optimization was done successfully which maximizes the heavy metals removal efficiencies at the same time minimizing the consumption.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In this work, pulsed-electrokinetic remediation study was carried out to investigate the effect of voltage gradient, bentonite/clay ratio and pulse the duty cycle on the overall heavy metals removal efficiencies, energy consumption. It also investigates the effect of these aforementioned independent variables on some important parameters which includes soil pH and electrical conductivity. Predictive models were successfully developed which help more in explaining the variation amongst the parameters of concern. Optimization was also performed which maximize the heavy metals removal efficiency at minimum energy consumption possible.

6.1 CONCLUSIONS

Based on the findings of this research, the following conclusions were drawn:

1. Increase in voltage gradient increases energy consumption as well as removal efficiency. Increase in the removal efficiency is as result of increase in mobility of ions due to rise in potential difference. However, decrease in removal efficiency of contaminant with high concentration of anions was observed with an increase in voltage gradient due to electro-osmotic flow moving in counter direction.

2. Increase in pulse duty cycle has increased the removal efficiency and energy consumption. This implies pulsing has not reduce overall energy consumption which is due to pulsing that was done in hours instead of seconds or milliseconds
3. Different types of predictive models were successfully generated for heavy metals (Cr, Cd, Cu, Hg and Pb) removal efficiencies and energy consumption with voltage gradient, Bentonite and clay ratio and pulse duty cycle as factors.
4. It was observed based on the 3D plots of all the studied responses that increase in Bentonite ratio decreases the removal efficiency due to its high surface area which promotes adsorption.
5. The process was numerically optimized which minimizes the energy consumption to 0.74kwh (308kwh/m^3 of treated soil) making it competitive.
6. Increase in voltage gradient was found to increase the soil electrical conductivity, this is due to increase in rate of anolyte and catholyte decomposition leading to production of more mobile Na^+ and OH^- ions that increases the electrical conductivity.
7. Increase in Voltage gradient was also found to increase the soil pH which is as well due to high rate of electrolyte decomposition leading to more basic front moving into the soil thereby raising the pH.
8. Soil Electrical conductivity was found to increase continuously with treatment time due to continuous refill and replacement of process fluids as they degrade which are the key sources of ions (Na^+ and NO_3^-) that increase the conductivity.

6.2 RECOMMENDATIONS

Based on the outcome of this research, the following are recommended:

1) Using the optimal values of factors generated, an experiment should be done in order to investigate the effect of pulsing in seconds and millisecond.
2) Different concentration of process fluids can be investigated to optimize the concentration.
3) Different electrode materials should also be investigated so as to select the best and affordable electrode that will improve the treatment process
4) Chelating agents should also be tried at the optimal conditions so as to further improve the treatment efficiencies.

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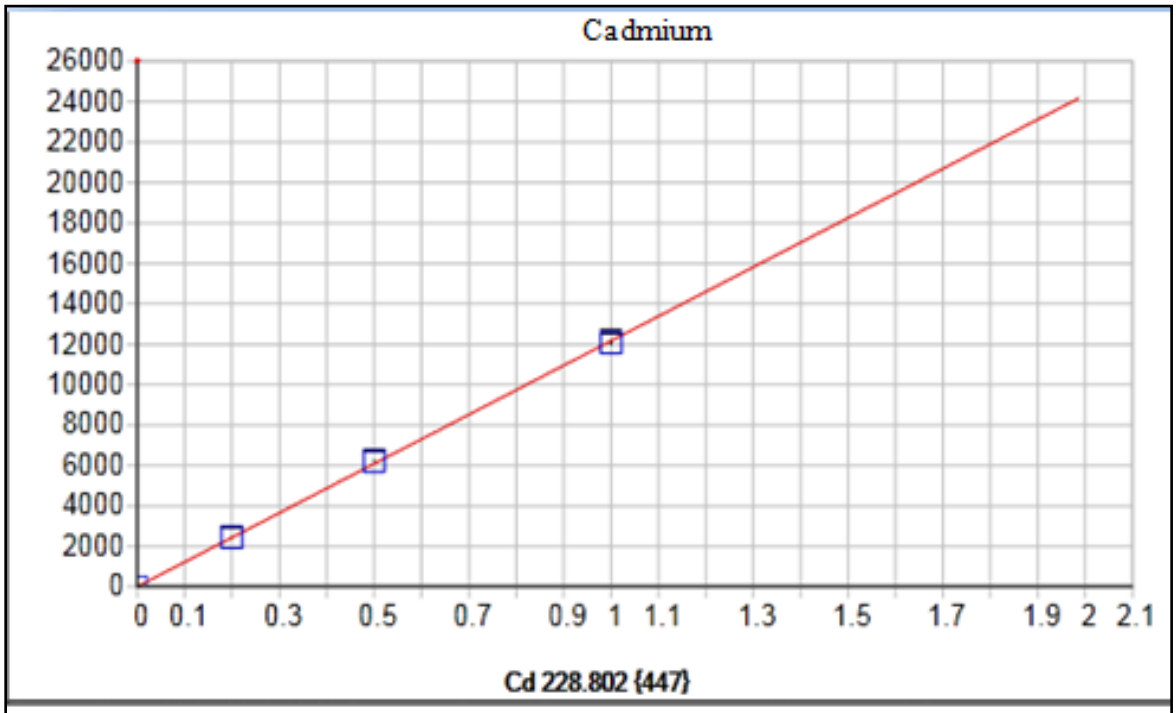
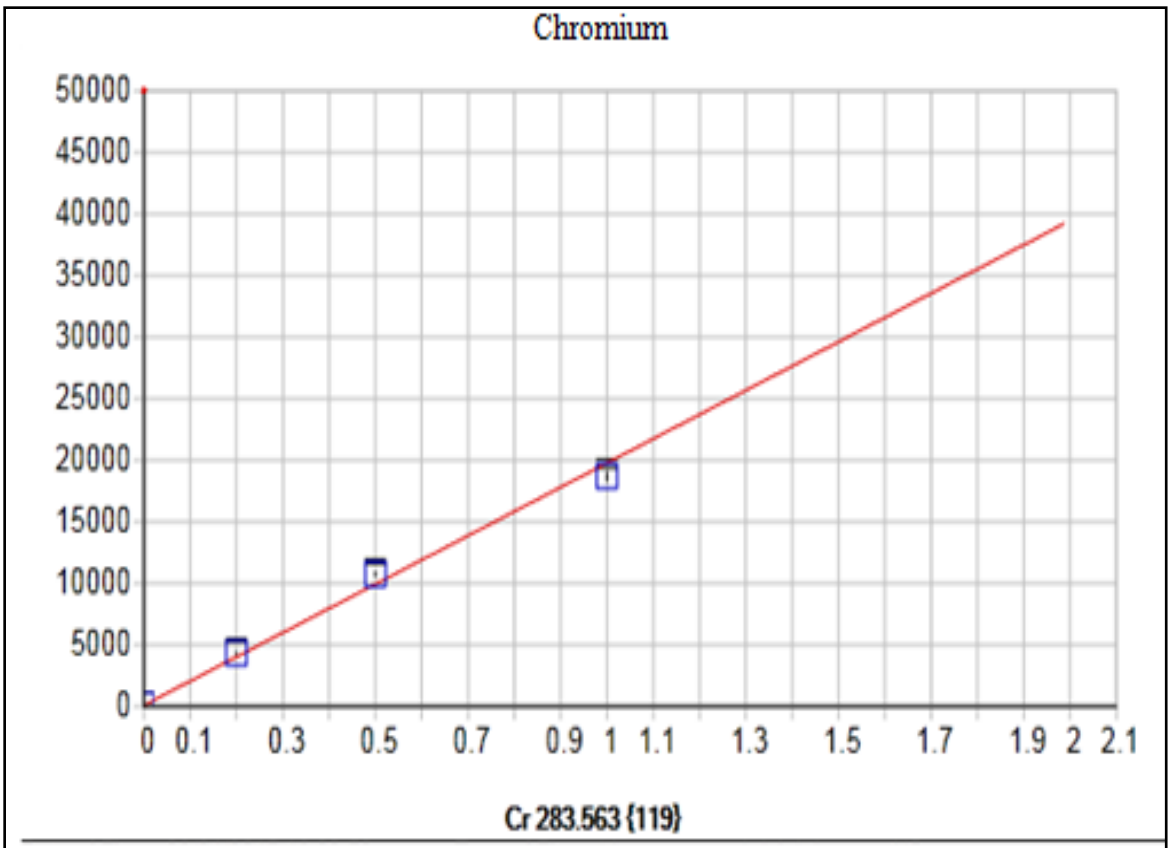
APPENDIX

Calibration Curves



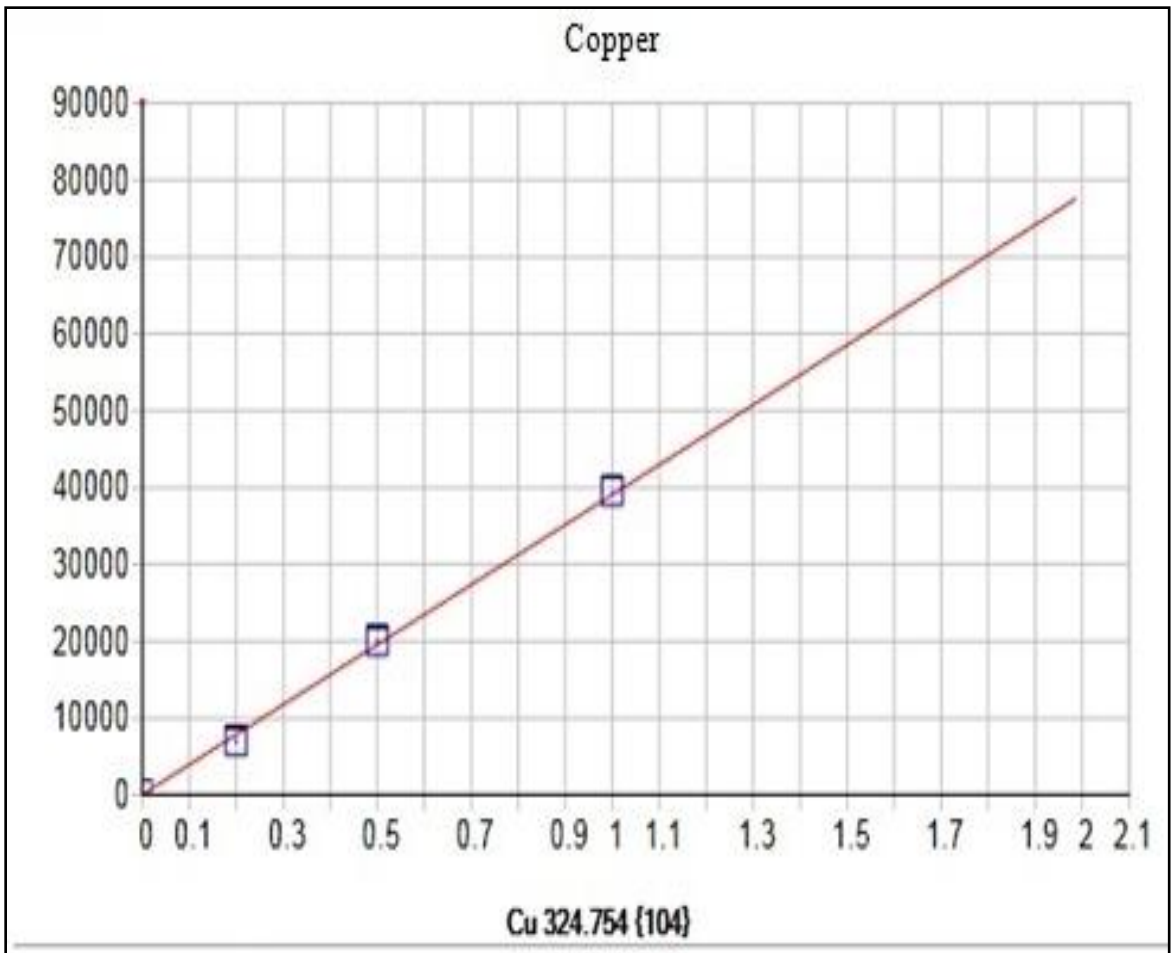
A0 (Offset):	3.432172	Re-Slope:	1.000000
A1 (Gain):	12167.95541	Y-int:	0.000000
A2 (Curvature):	0.000000		
n (Exponent):	1.000000		
Correlation:	0.999919	Status:	OK.
Std Error of Est:	4.045790		
Predicted MDL:	0.000075		
Predicted MQL:	0.000249		

Std. Name	Stated Conc.	Found Conc.	Difference	% Diff.	(S)IR	Std Dev	Emphasis
Blank	.00000	-.00000	-.000	.000	3.4195	.529	1
CalibStd-1	.20000	.19883	-.001	-.584	2422.8	17.8	1
CalibStd-2	.50000	.50986	.010	1.97	6207.4	25.0	1
CalibStd-3	1.0000	.99131	-.009	-.869	12066.	96.3	1



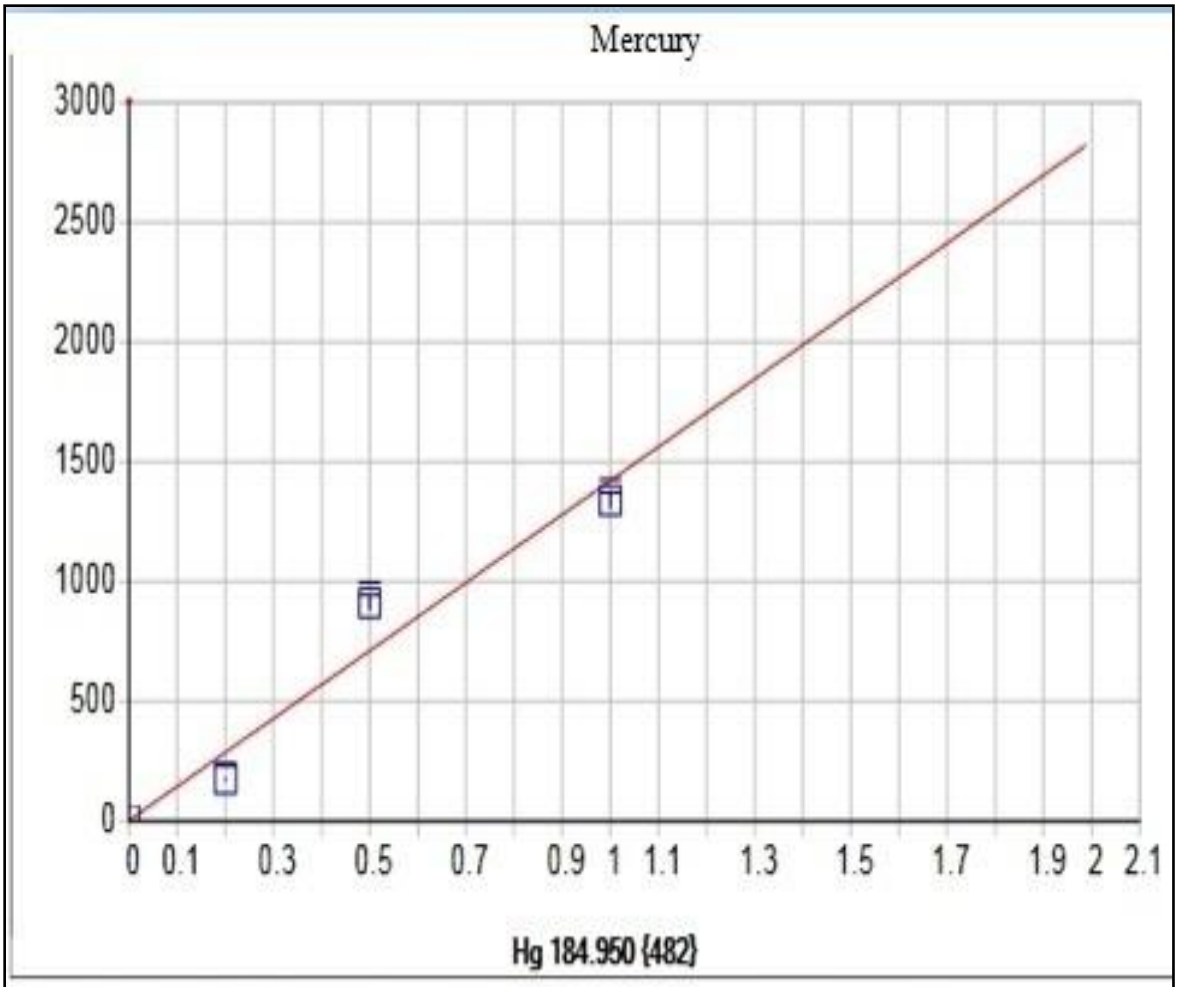
A1 (Gain):	19688.24422	Y-int:	0.000000
A2 (Curvature):	0.000000		
n (Exponent):	1.000000		
Correlation:	0.997723	Status:	OK
Std Error of Est:	34.660039		
Predicted MDL:	0.000175		
Predicted MQL:	0.000583		

Std. Name	Stated Conc.	Found Conc.	Difference	% Diff.	(S)IR	Std Dev	Emphasis
Blank	.00000	-.00002	-.000	.000	108.48	9.56	1
CalibStd-1	.20000	.21526	.015	7.63	4347.0	83.5	1
CalibStd-2	.50000	.54124	.041	8.25	10765.	176.	1
CalibStd-3	1.0000	.94350	-.057	-5.65	18685.	337.	1



A0 (Offset):	86.316331	Re-Slope:	1.000000
A1 (Gain):	38996.52933	Y-int:	0.000000
A2 (Curvature):	0.000000		
n (Exponent):	1.000000		
Correlation:	0.999142	Status:	OK
Std Error of Est:	42.097359		
Predicted MDL:	0.000117		
Predicted MQL:	0.000389		

Std. Name	Stated Conc.	Found Conc.	Difference	% Diff.	(S)IR	Std Dev	Emphasis
Blank	.00000	.00002	.000	.000	86.932	15.1	1
CalibStd-1	.20000	.17747	-.023	-11.3	7007.1	219.	1
CalibStd-2	.50000	.51120	.011	2.24	20021.	200.	1
CalibStd-3	1.0000	1.0113	.011	1.13	39525.	30.1	1



A0 (Offset):	2.765614	Re-Slope:	1.000000
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A2 (Curvature):	0.000000		
n (Exponent):	1.000000		
Correlation:	0.979280	Status:	OK
Std Error of Est:	7.635821		
Predicted MDL:	0.000324		
Predicted MQL:	0.001079		

Std. Name	Stated Conc.	Found Conc.	Difference	% Diff.	(S)IR	Std Dev	Emphasis
Blank	.00000	.00004	.000	.000	2.8156	.463	1
CalibStd-1	.20000	.12140	-.079	-39.3	174.90	3.94	1
CalibStd-2	.50000	.63817	.138	27.6	907.61	26.0	1
CalibStd-3	1.0000	.94043	-.060	-5.96	1336.2	28.1	1

Appendix A: Weekly Soil Electrical Conductivity (mS/cm)

RUNS	Factors			Initial	Week 1	Week 2	Week 3
	B/C	P.D.C	V.G				
R1	0.3	0.2	0.9	8.860	13.263	16.050	17.950
R2	0.3	0.6	0.5	9.700	20.253	17.937	21.643
R3	0.3	0.2	0.5	9.180	11.387	14.867	18.423
R4	0.3	0.6	0.9	9.750	17.053	14.573	21.480
R5	0.5	0.4	0.9	8.070	19.800	20.487	22.140
R6	0.1	0.6	0.7	12.500	20.920	20.457	27.550
R7	0.1	0.2	0.7	10.630	13.623	16.353	18.573
R8	0.1	0.4	0.5	12.760	18.253	20.980	21.157
R9	0.3	0.4	0.7	9.910	18.370	21.353	21.157
R10	0.1	0.4	0.9	11.550	19.950	23.217	25.113
R11	0.5	0.2	0.7	6.660	9.543	14.080	18.607
R12	0.5	0.4	0.5	8.070	18.597	20.547	24.190
R13	0.5	0.6	0.7	7.500	19.443	16.343	22.463

Appendix B: Weekly Soil pH

RUNS	Factors			Weekly Soil pH			
	B/C	PDC	V.G	Initial	Week 1	Week 2	Week 3
R1	0.3	0.2	0.9	8.270	9.673	9.563	9.927
R2	0.3	0.6	0.5	8.400	12.177	12.503	12.360
R3	0.3	0.2	0.5	8.270	8.960	10.147	10.277
R4	0.3	0.6	0.9	8.400	11.860	12.140	12.217
R5	0.5	0.4	0.9	8.600	10.293	10.420	11.437
R6	0.1	0.6	0.7	8.200	12.280	12.460	12.413
R7	0.1	0.2	0.7	8.080	8.683	9.310	9.197
R8	0.1	0.4	0.5	8.270	9.687	11.120	10.087
R9	0.3	0.4	0.7	8.330	10.013	11.403	11.653
R10	0.1	0.4	0.9	8.130	10.210	11.330	11.947
R11	0.5	0.2	0.7	8.390	9.173	9.613	9.707
R12	0.5	0.4	0.5	8.600	10.623	10.393	11.400
R13	0.5	0.6	0.7	8.600	12.123	12.277	12.313

Appendix C: Weekly Soil Moisture Content (%)

	Factors			Weekly Soil Moisture Content (%)			
	B/C	PDC	V.G	Initial	Week 1	Week 2	Week 3
R1	0.3	0.2	0.9	49.000	47.667	45.667	46.000
R2	0.3	0.6	0.5	50.000	47.333	47.000	48.000
R3	0.3	0.2	0.5	49.000	47.667	45.667	46.333
R4	0.3	0.6	0.9	49.000	46.333	46.333	47.667
R5	0.5	0.4	0.9	54.000	51.333	49.667	50.000
R6	0.1	0.6	0.7	47.000	44.667	44.000	45.000
R7	0.1	0.2	0.7	47.000	46.000	44.333	43.000
R8	0.1	0.4	0.5	47.000	45.000	42.333	44.000
R9	0.3	0.4	0.7	50.000	47.667	46.000	48.000
R10	0.1	0.4	0.9	48.000	44.667	44.000	46.000
R11	0.5	0.2	0.7	53.000	52.000	51.333	51.333
R12	0.5	0.4	0.5	54.000	54.333	51.000	53.000
R13	0.5	0.6	0.7	53.000	52.333	51.333	53.000

Appendix D: Average Weekly Electric Current (A)

Runs	Factors			Average Weekly Electric Current (A)		
	B/C	PDC	V.G	Week 1	Week 2	Week 3
R1	0.3	0.2	0.9	0.2346	0.2222	0.2000
R2	0.3	0.6	0.5	1.1385	1.3185	1.3500
R3	0.3	0.2	0.5	0.2231	0.2296	0.2214
R4	0.3	0.6	0.9	1.1035	1.2628	1.2927
R5	0.5	0.4	0.9	0.6692	0.7481	0.7616
R6	0.1	0.6	0.7	1.2654	1.3315	1.3524
R7	0.1	0.2	0.7	0.2635	0.2583	0.2494
R8	0.1	0.4	0.5	0.5615	0.5926	0.6291
R9	0.3	0.4	0.7	0.5308	0.5944	0.6628
R10	0.1	0.4	0.9	0.6231	0.6889	0.7547
R11	0.5	0.2	0.7	0.2481	0.2602	0.2613
R12	0.5	0.4	0.5	0.5654	0.6574	0.6733
R13	0.5	0.6	0.7	1.2846	1.4130	1.3845

Appendix E: Average Weekly Cumulative Electroosmotic Volume (cm^3)

Runs	Factors			Average Cumulative Weekly Electroosmotic Volume (cm^3)		
	B/C	PDC	V.G	Week 1	Week 2	Week 3
R1	0.3	0.2	0.9	271.950	443.100	537.500
R2	0.3	0.6	0.5	368.900	700.000	975.000
R3	0.3	0.2	0.5	150.850	443.100	540.000
R4	0.3	0.6	0.9	648.830	1215.900	1822.500
R5	0.5	0.4	0.9	616.525	1109.640	1401.628
R6	0.1	0.6	0.7	452.200	824.600	1147.500
R7	0.1	0.2	0.7	231.525	414.820	522.500
R8	0.1	0.4	0.5	226.170	526.330	630.000
R9	0.3	0.4	0.7	511.700	984.900	1242.907
R10	0.1	0.4	0.9	382.305	744.100	920.581
R11	0.5	0.2	0.7	290.850	482.300	645.000
R12	0.5	0.4	0.5	366.100	725.900	886.395
R13	0.5	0.6	0.7	675.500	1218.000	1732.500

Appendix F: Average Weekly Energy Consumption (kwh/m^3 of Soil Treated)

Runs	Factors			Weekly Energy Consumption (kwh/m^3 of Soil Treated)		
	B/C	PDC	V.G	Week 1	Week 2	Week 3
R1	0.3	0.2	0.9	59.123	112.000	151.200
R2	0.3	0.6	0.5	478.154	1107.556	1701.000
R3	0.3	0.2	0.5	31.231	64.296	93.000
R4	0.3	0.6	0.9	834.217	1909.320	2931.930
R5	0.5	0.4	0.9	337.292	754.133	1151.581
R6	0.1	0.6	0.7	744.046	1565.822	2385.600
R7	0.1	0.2	0.7	51.638	101.267	146.650
R8	0.1	0.4	0.5	157.231	331.852	528.419
R9	0.3	0.4	0.7	208.062	466.044	779.442
R10	0.1	0.4	0.9	314.031	694.400	1141.033
R11	0.5	0.2	0.7	48.623	101.993	153.650
R12	0.5	0.4	0.5	158.308	368.148	565.535
R13	0.5	0.6	0.7	755.354	1661.644	2442.300

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